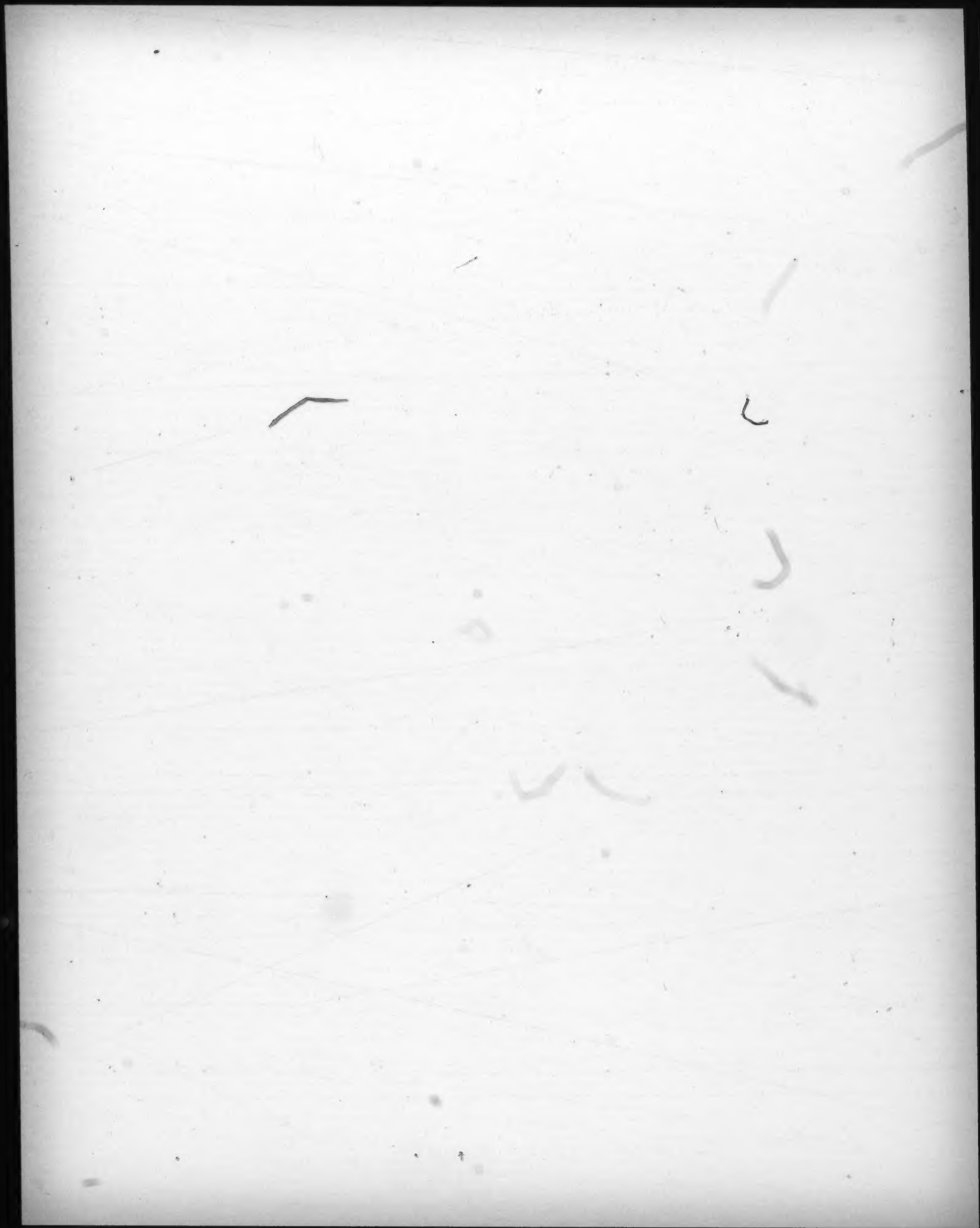


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Evaluation of Rhenium-Osmium (Re-Os) Geochronology of Pyrite, Sphalerite, and Arsenopyrite: Examples from the Red Dog Zn-Pb-Ag Deposit, Alaska, and the Meguma Group Gold Deposits, Nova Scotia.

by

Ryan Michael Morelli



A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of *Masters of Science*.

Department of Earth and Atmospheric Sciences

Edmonton, Alberta
Fall 2003.



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Abstract:

Re-Os geochronology was performed on main stage pyrite and sphalerite from the Red Dog Pb-Zn-Ag deposit, Alaska, and arsenopyrite from Meguma Gold Deposits (MGD), Nova Scotia, to determine ore formation ages. Red Dog pyrite yields a Re-Os isochron age of 338.3 ± 5.8 Ma, identical to independent age constraints, whereas sphalerite yields an inaccurate age, demonstrating that sphalerite Re-Os isotopic compositions are easily disturbed. MGD arsenopyrite from bedding-parallel veins at The Ovens deposit yield a Re-Os isochron age of 408.6 ± 4.5 Ma, whereas bedding-discordant veins at this deposit yield a concomitant single-mineral model age (406.9 ± 1.7 Ma). Saddle-reef vein arsenopyrite from the Dufferin deposit yield precise Re-Os isochron and model ages clustering at 381 Ma. These results indicate either a diachronous migration of Acadian orogenesis across the Meguma Terrane, or a later influx of mineralizing fluids, and show the utility of the Re-Os arsenopyrite chronometer for dating gold mineralization.

*This thesis is dedicated to Lia and Vincent, my inspiration and motivation, and to my
parents, for their unending love and support.*

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First and foremost, I would like to thank Lia and Vincent for their love and belief in me – I couldn't do it without you. Much appreciated are my mom, dad, brother, and sister for their love, guidance, and encouragement. Likewise, the Stolte family is thanked for their love and support. I am much indebted to my supervisor, Dr. Robert Creaser, for all that he has taught me over the past two years, and for always making sure that my and my family's best interests are being considered. Dr. David Selby is thanked for providing my laboratory training, for continually teaching me new things, for answering my stupid questions, and for letting me play on his soccer (I mean 'football') team. Thanks are due to Stacey Hagen and Kelly Nixon for their hard work in the labs, for always helping me out when I'm in need, and for being all-around great co-workers. For making the U of A an enjoyable place to work on a daily basis, I would like to thank my friends and colleagues at the U of A, most especially Brian, Russell, Trevor, Rajeev, Yvon, James, Carlos, Alex, and Christian (let's face it man – you might as well be paying tuition here!). On a similar note, I would like to thank Dave MacDougall, Ralf Maxeiner, Bruno Lafrance, and Ken Ashton for their guidance and tutelage in the 'early years', but most of all for being and continuing to be great friends.

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List of Abbreviations and Symbols:

Ma	mega annum (million years)
MGD	Meguma Gold Deposits
XRD	x-ray diffraction
μ l	microlitre
pg	picogram
MSWD	mean square of weighted deviates
ppb	parts per billion
ppt	parts per trillion
$2\sigma_m$	2 sigma mean

Chapter 1 – Introduction

In the past, one of the foremost obstacles hampering the comprehensive modeling of ore deposit formation has been the inability to conclusively determine the absolute age of ore mineralization. This study was designed to address this problem by further developing the use of the Re-Os chronometer with ore sulfides, and/or sulfides paragenetically related to ore minerals. The principal advantage of the Re-Os system over other isotope systems for this application lies in the chalcophile nature of both Re and Os. This characteristic permits dating of the sulfidic ore minerals directly, rather than relying on dates from associated silicate minerals from which temporal and genetic relationships to ore must often be inferred.

Previous studies of Re-Os sulfide geochronology have focused primarily on molybdenite (e.g. Torrealday, 2000; Watanabe and Stein, 2000; Stein et al., 2001; Selby and Creaser, 2001a, b; Selby et al., 2002). This mineral, having characteristically high concentrations of Re and negligible common Os, has been proven an extremely robust and reliable chronometer (e.g. Stein et al., 2001). Other studies (Stein et al., 1998, 2000; Mathur et al., 1999; Morgan et al., 2000; Arne et al., 2001; Kirk et al., 2002) have attained some success in applying the Re-Os method to sulfides with much lower Re and Os abundances, including pyrite and arsenopyrite. However, despite an ability to produce ostensibly meaningful ages, many of these studies fail to adequately exhibit the degree of accuracy of the determined Re-Os sulfide ages with respect to independent temporal constraints. Furthermore, they do not sufficiently address several important issues pertaining to analytical protocol, isotope systematics, and general advantages and limitations of the Re-Os isotopic system with respect to pyrite and arsenopyrite

geochronology. Such issues must be resolved in order to validate these 'low-level' (Stein et al., 2000) sulfides as reliable and robust candidates for Re-Os geochronology.

The present study more rigorously evaluates the usefulness of the Re-Os system for accurately dating pyrite, arsenopyrite, and, for the first time, explores the potential of sphalerite as a chronometer using the Re-Os isotope system. This objective is accomplished by means of a two-stage approach:

- 1) The accuracy of the Re-Os pyrite and sphalerite geochronometers are tested through a comparison of the determined Re-Os age(s) to the existing temporal constraints for main stage ore from the world-class Red Dog sedimentary-hosted Zn-Pb-Ag deposit, in the northern Cordillera of Alaska, U.S.A. (Fig.1). This deposit is the largest producer of Zn worldwide, with estimated ore reserves of 142 million tonnes (16.6% Zn, 4.3% Pb), and is one of several shale-hosted base metal deposits in the Brooks Range Zn-Pb-Ag Belt of the northern Cordillera (Fig.1). Main stage ore at Red Dog is characterized by two principal ore occurrences; massive sulfide ore and cross-cutting vein ore. The age of Red Dog massive ore is biostratigraphically bracketed by the host rocks (Middle Carboniferous - Meramecian to early Chesterian (ca. 340 – 320 Ma; Dumoulin et al., 2004), and several $^{40}\text{Ar}/^{39}\text{Ar}$ dates from mica in regional lithologies (Werdon et al., 1997), thus providing an excellent check for Re-Os geochronology. However, the age and origin of vein ore mineralization is presently debated, and a peripheral aim of the study is to conclusively resolve the temporal relationship between these two ore facies, thus allowing the evaluation of the ore-forming events to be accurately placed into the regional geologic framework.

2) The feasibility of the 'low-level' (i.e. low Re concentration) Re-Os sulfide chronometer to pinpoint precise Au mineralization ages of deposits that are historically difficult to date is evaluated through Re-Os chronometry of arsenopyrite genetically associated with vein-hosted Au from the Meguma Gold Deposits (MGD), Meguma Terrane, Nova Scotia, Canada (Fig.3). The MGD, collectively having produced ~37 million grams of Au, are an ideal candidate for this portion of the study, as current constraints on the timing of mineralization are broad, and the exact timing of gold mineralization is ardently debated. As such, a precise Re-Os age within these broad constraints would effectively resolve the age of mineralization, and may provide more robust constraints on models of Au mineralization. Additionally, as the MGD are widely hypothesized to have formed during a distinct stage of orogenesis, mineralization age resolution may provide insight into the timing of orogenic activity in different regions of the Meguma Terrane.

This methodology will provide the most comprehensive evaluation of the pyrite, sphalerite, and arsenopyrite Re-Os chronometers to date, and will conclusively establish their potential for dating ore mineralization. In doing so, this study will also advance current analytical protocol for performing Re-Os sulfide geochronology, further explore the use of Os isotopes for tracing ore sources, examine the distribution of Re and Os isotopes within these sulfide minerals, and investigate the use of the technique for dating processes responsible for ore formation.

Despite showing exceptional potential for dating mineralization events, the siderophile-chalcophile affinity of the Re-Os isotopic system precludes it as an ideal method of dating events associated predominately with silicate-dominated mineralogy

(e.g. emplacement ages of igneous rocks). Furthermore, as research showing the potential applications of Re-Os sulfide geochronology is in its early stages, many potential limitations are yet unresolved. For example, closure temperatures of common sulfide minerals with respect to retention of the parent and daughter elements remains very loosely constrained. As well, the ideal sample size for Re-Os analysis, which is likely mineral-dependant, is currently unresolved and a methodology for extracting sufficient amounts of disseminated sulfide from the host rock is yet to be established. Hence, in spite of significant analytical and theoretical advances made in this study for Re-Os sulfide geochronology, much work remains to be done to ascertain the full potential of this method.

This thesis is presented in a mixed (traditional and paper) format. This is due primarily to the fact that all work pertaining to Re-Os sulfide geochronology of the Red Dog deposit has been submitted to Economic Geology for publication in an upcoming special issue devoted to the Red Dog deposit, whereas work on the Meguma Group deposits have yet to be submitted for publication at the time of thesis submittal. All sections in this thesis pertaining to the Red Dog deposit, excluding parts of the introduction and the conclusion, were taken verbatim from the submitted Economic Geology paper. Editorial work on this paper was performed by three of the coauthors (Dr. Robert Creaser and Dr. David Selby, University of Alberta, and Dr. Karen Duttweiler Kelley, United States Geological Survey). The remainder of work on the Red Dog project was performed by the author of this thesis.

Chapter 2 - Geological Setting of Study Areas:

a) Red Dog:

Regional Geology:

The Brooks Range of Alaska is an east-west trending fold and thrust belt at the northern extension of the North American Rocky Mountain system. The positioning of the belt into its present orientation occurred during the Middle Jurassic to Cretaceous Brookian Orogeny, interpreted by some to be contemporaneous with the opening of the Canada Basin (Lawver and Scotese, 1990). The Red Dog base metal deposits are located in the De Long Mountains in the northwestern Brooks Range (Fig. 1). The regional geology is characterized by a series of stacked and fault-bounded age-equivalent allochthons (Tailleur 1966; Martin 1970; Mull, 1982; Mayfield et al., 1988), thought to represent parts of formerly continuous sedimentary basins that were structurally emplaced during Brookian orogenesis. The Red Dog deposits and others like them in the western and central Brooks Range are all within the Endicott Mountains allochthon (Mull, 1982), one of the structurally lowest allochthons in the western Brooks Range (Moore et al., 1986).

The stratigraphy of the Endicott Mountains allochthon near Red Dog includes the Endicott Group, Lisburne Group, Etivluk Group, Ipewik unit and Okpikruak Formation (Fig. 2).

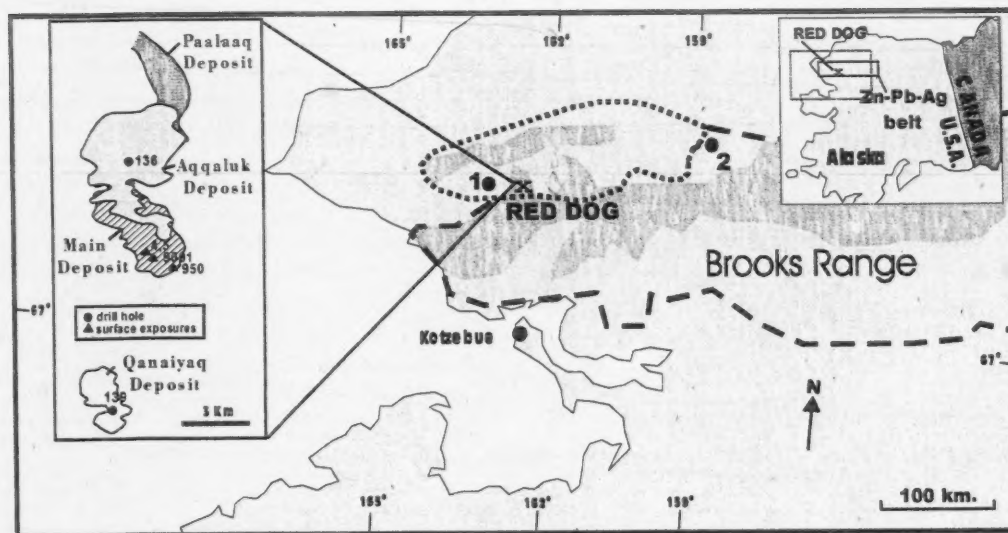


Figure 1: Location of the Red Dog deposit in the DeLong Mountains, northern Cordillera, northwestern Alaska (modified from Moore et al., 1994). Extent of the Brooks Range is denoted by dashed line, extent of DeLong Mountains is denoted by dotted line; dark shaded region indicates extent of Endicott Mountains Allochthon; 1 and 2 indicate location of Su-Lik and Drenchwater Creek deposits, respectively (figure modified from Moore et al., 1994, except for Red Dog deposits inset, which is modified from Young, 2004).

This stratigraphy reflects the progressive rifting of a passive continental margin and the concurrent deposition of sediment on a subsiding continental slope (Mayfield et al., 1988) or in an oceanic basin (Churkin et al., 1979; 1980). Deposition evolved from non-marine continental shelf deposits in the late Devonian, to carbonate platform and age-equivalent anoxic basinal facies, and finally to more oxidizing marine deposits by the Pennsylvanian. The lowermost stratigraphic unit in the sequence is the Upper Devonian to Lower Mississippian Endicott Group. In the Red Dog region, the base of the Endicott Group consists of the Hunt Fork shale and overlying Noatak sandstone, representing deposition in a shallow marine setting (Mayfield et al., 1988). The Noatak Sandstone is conformably overlain by the Upper Devonian and Lower Mississippian Kanayut Conglomerate, a fluvial-deltaic sequence (Nilsen and Moore, 1984). During the Early Mississippian, the coarse clastic section was succeeded by shallow-water, fine-grained marine deposits of the Kayak Shale, which comprise black shale and minor fossiliferous limestone. In the western Brooks Range, the Kayak Shale is overlain by black carbonaceous shale, carbonate, and chert of the Mississippian Kuna Formation (Mull et al., 1982); the basinal facies that is correlative with the platform carbonate rocks of the Lisburne Group further east. The Kuna Formation, host to the Red Dog deposits, is subdivided into the lower Kivalina unit and the overlying Ikalukrok unit (Moore et al., 1986). The former consists of calcareous shale, calcareous spiculite, and bioclastic grainstone and packstone and contains only trace amounts of base metal mineralization, whereas the latter hosts the predominance of base metal mineralization, and is comprised of siliceous shale, mudstone, calcareous radiolarite, and calcareous lithic turbidite (Dumoulin et al., 2004)

with sparse intercalated igneous flows and intrusions (Nokleberg and Winkler, 1982, Lange et al., 1985).

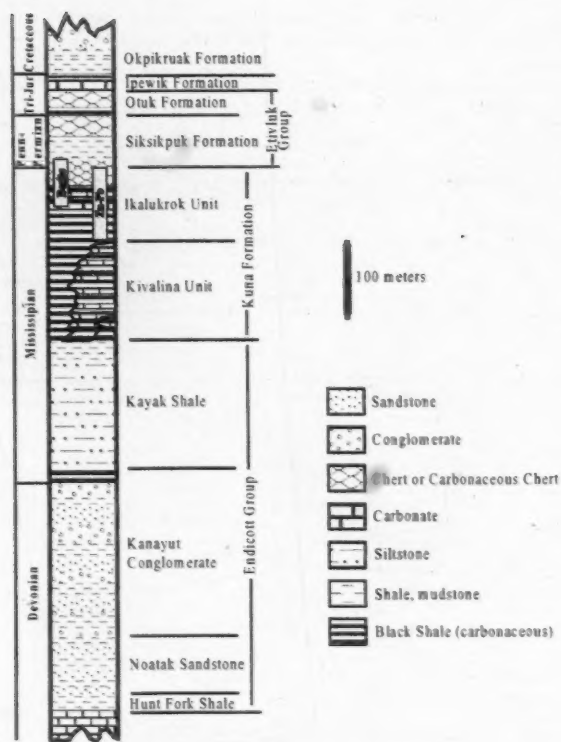


Figure 2: Representative stratigraphy of region near Red Dog deposits (modified from Young, 2004).

A distinctive orange chert bed (Orange Cherty Unit; Moore, 1986) marks the transition from a predominately reducing depositional environment in rocks of the Kuna Formation to oxidizing conditions in the overlying Siksikpuk Formation (Mull et al., 1982). The Siksikpuk Formation is the lower of two formations that comprise the Pennsylvanian to Middle Jurassic Etivluk Group, and consists of pyritic and baritic shale and chert. The Otuk Formation, the uppermost unit of the Etivluk Group, conformably overlies the Siksikpuk Formation, and consists primarily of black shale, chert, and limestone. The Jurassic to Lower Cretaceous Ipewik Formation unconformably overlies the Otuk Formation, and consists of marine deposits of shale, limestone, and quartz-rich sandstone. The unconformable Lower Cretaceous Okpikruak Formation, the youngest stratigraphic interval present within the Endicott Mountain allochthon in the Red Dog area, is characterized by a thick sequence of clastic sedimentary rocks derived from the onset of regional uplift during the Brookian Orogeny.

Red Dog Deposit Geology:

Four distinct deposits occur in the Red Dog mine area, including from south to north the Qanaiyaq, Main, Aqqaluk, and Paalaaq deposits (Fig. 1). The structure in the mine area emulates that of the regional geology, in that it consists of a series of stacked orebodies that occur in relatively small thrust sheets, or 'plates', that formed during Brookian deformation. The stacked orebodies get successively deeper from south to north. The Main deposit is the highest grade of the four and is the only one currently in production. Reconstructions of the undeformed ore bodies (Plahuta and Robinson, 1978; Lange et al., 1985; Young, 1989; Sims, 1996; Edgerton, 1997) reveal that much of the

main stage ore is stratabound within Ikalukrok unit siliceous shale and carbonate. Most ore is present as a poorly-bedded to massive stratabound lens; sphalerite, galena, and pyrite/marcasite are the dominant sulfide minerals present. The massive ore grades up to sulfide-bearing barite that in turn grades to sulfide-poor barite at the top (Young, 1989; Schmidt, 1997). All of the deposits straddle the boundary between Ikalukrok unit and the Siksikpuk Formation.

Edgerton (1997) proposed that each deposit represents a distinct vent site or zone of focused discharge. Based on textural variations and geochemical zoning from south to north between deposits, Kelley et al. (2004) suggest that the four deposits were actually one relatively continuous mineralizing system, with Aqqaluk and Paalaaq being distal and Qanaiyaq and Main more proximal to the main site of focused fluid flow.

In general terms, stratabound main stage ore at Red Dog is characterized by two main types, massive sulfide ore and sulfide vein ore. These, and less significant ore facies present at Red Dog, are well documented (e.g. Lange, 1985; Moore et al., 1986; Edgerton, 1997; Kelley et al., 2004), and the reader is referred to these publications for a more comprehensive description of the various styles of ore mineralization. The mineralogical and textural characteristics of the Main deposit were interpreted by Sims (1996) to represent a large vent complex with an extensively developed underlying feeder pipe system. Kelley et al. (2004) agree that the complex textural variations within the Main deposit suggest that it must have been at or near the site of focused fluid flow. However, they suggest that some of the ore textures used to argue that the Main deposit was a vent complex or feeder pipe system may have formed by other processes, such as replacement of carbonate, hydrothermal recrystallization of barite by metal-bearing fluids, or later

replacement of barite in the deposits by quartz. Massive sulfide ore is stratiform and relatively non-bedded, and exhibits a complex assemblage of replacement, fragmental, and brecciation textures. Several lines of evidence, most notably the presence of sedimentary structures (Moore et al., 1986), the existence of a vent fauna (Young, 1989), and textural variations of barite and sulfide in the deposit (Schmidt, 1997, and references therein; Kelley et al., 2004) indicate that this ore facies is, in part, synsedimentary to syndiagenetic in origin.

Sulfide veins at Red Dog are steeply-dipping and discordant with respect to the host Ikalukrok shale, massive sulfide ore, and silica rock. Sulfide phases within the veins are normally coarse-grained and exhibit textures indicative of growth in open spaces. Sphalerite is the most common sulfide mineral present, with lesser amounts of galena and pyrite/marcasite.

The sulfide veins at Red Dog are similar in many respects to regional occurrences of sulfide-rich veins and vein-breccias that are stratabound within clastic rocks of the Endicott Group, particularly within the Noatak sandstone or Kanayut conglomerate (Werdon et al., 1997; Kelley et al., 2000). The clastic rocks and associated sulfides underlie the Kuna Formation that hosts the stratabound massive sulfide deposits like those at Red Dog. One of these clastic hosted vein occurrences is located about 10 km east of the Red Dog deposits, and numerous others occur along a belt that extends for 250 km to the east. These occurrences are characterized primarily by banded sulfides (sphalerite, galena, and pyrite/marcasite with rare chalcopyrite) in veins and sulfide-bearing breccias. Where observed in outcrop, the veins are sharply discordant with host rocks. Studies concerning the clastic-hosted veins (Werdon, 1997; Kurtak et al., 1995)

demonstrate that they formed predominately during Mississippian time, and that minor remobilization of sulfides into Mesozoic structures has also occurred. The exact relationship between these clastic-hosted veins and vein ore at Red Dog is unknown. Mineralogical, geochemical and isotopic similarities between the clastic-hosted veins and sulfide veins at Red Dog argue for a similar origin of formation during the Carboniferous (Kelley et al., 2000; Young, 1989; Weldon, 1997; Ayuso et al., 2004). An alternative hypothesis is that the sulfide veins formed during Late Jurassic time in rocks that underwent brittle deformation during Brookian orogenesis. This model envisages the vein sulfides forming due to remobilization of metals from older disseminated sources, and re-emplacement into Mesozoic fractures and brecciated zones (Ellersieck et al., 1990; Kurtak et al., 1995). Re-Os sulfide geochronology is used in this study to directly test if the vein ore at Red Dog is (1) approximately coeval with the massive sulfide mineralizing event, (2) a separate, late pulse of mineralization, or (3) if the vein ore was emplaced or locally remobilized from surrounding massive ore during Mesozoic deformation.

b) Meguma Gold Deposits:

Regional Geology:

The Meguma Terrane, the easternmost accreted terrane of the northern Appalachians, is confined to and comprises most of mainland Nova Scotia, Canada (Fig. 3). The formation of the northern Appalachians occurred as a result of three distinct orogenic episodes; the Ordovician Taconic Orogeny, the Devonian Acadian Orogeny, and the Carboniferous Alleghanian Orogeny. Accretion of the Meguma Terrane to the Laurentian margin took place during the Acadian Orogeny, coeval with complete closure

of the Iapetus Ocean (Williams, 1995). The Meguma Terrane is juxtaposed with the adjacent Avalon Terrane along the former's northern boundary; the suture is represented by the steeply-dipping Cobequid – Chedabucto Fault Zone (Fig. 3). The Meguma Terrane is hypothesized to represent either the passive margin of the southern Avalon Terrane (Keppie and Dostal, 1991; Keppie et al., 1997) or a suspect terrane derived from either northwestern Africa (Schenk, 1970) or southwestern South America (Dalziel et al., 1994) that docked with the Avalon Terrane.

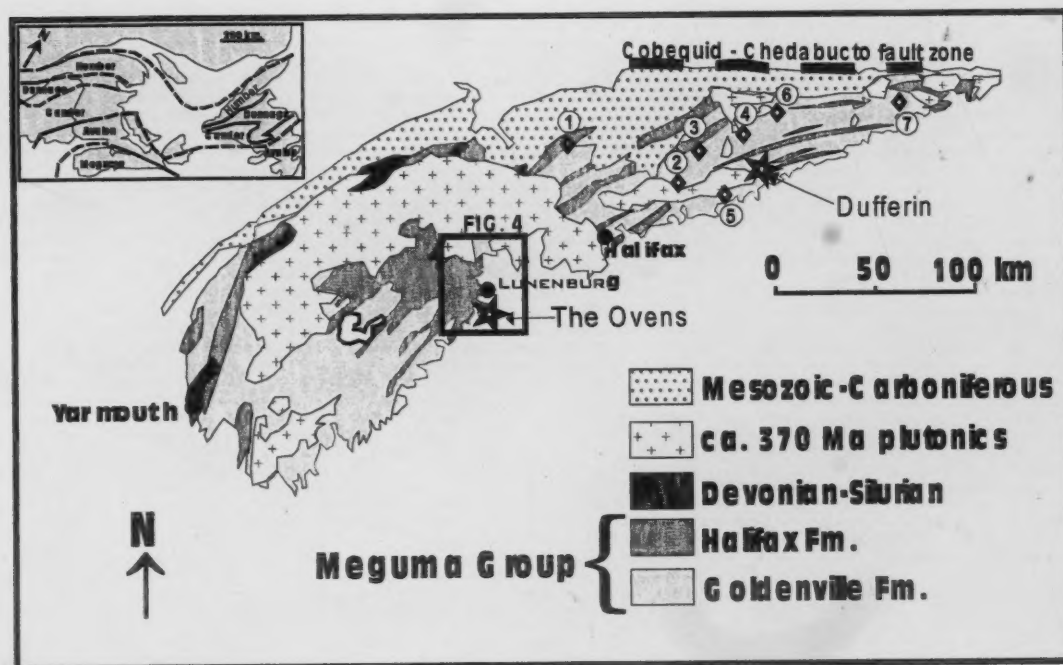


Figure 3: Generalized geology of the Meguma Terrane, Nova Scotia, Canada (after Hicks, 1999). Circled numbers denote location of other significant gold deposits in the Meguma Terrane: (1) West Gore, (2) Moose River (incl. Touquoy Zone), (3) Caribou, (4) Beaver Dam, (5) Tangier, (6) Fifteen Mile Stream, (7) Upper Seal Harbour.

The Meguma Group, consisting of >10 km of flysch deposits, comprises the major lithologic constituent of the Meguma Terrane, and is subdivided into two groups:

(1) the basal Goldenville Formation, and (2) the conformably overlying Halifax Formation. The Goldenville Formation is a Cambro-Ordovician sandstone-dominated unit with subordinate interbeds of shale, reflecting voluminous turbidite deposition in an abyssal plain fan (Schenk, 1970). The Ordovician Halifax Formation is comprised predominately of deep-water shales as part of a prograding continental-rise prism or prodeltaic wedge over the Goldenville sediments (Schenk, 1995). An additional siliciclastic unit, the Silurian – Lower Devonian Annapolis Group, is excluded from the Meguma Group, though this separation is viewed as artificial as both groups share similar post-depositional histories (Schenk, 1995).

The Meguma Group constitutes either a thin allochthonous sheet that was emplaced over younger autochthonous Avalonian basement rocks during Acadian orogenesis (Eberz et al., 1991; Clarke et al., 1993), or sediment deposited unconformably on Neoproterozoic Avalonian basement (Keppie and Dostal, 1991). The precise nature of the lower crust is uncertain, but is likely represented at surface by granulite facies xenoliths in late Devonian lamprophyre dykes, and by the ca. 370 Ma Liscomb Complex (Kontak and Reynolds, 1994); amphibolite-granulite facies gneisses and schists in the Meguma Group that are derived from underlying Avalonian crust (Clarke et al., 1993).

Deformation in the Meguma Terrane is characterized primarily by upright N-S to NE-SW trending, tight to open upright folds with shallowly-plunging hinges. The folds are generally chevron- to box-shaped, and were reactivated along bedding parallel horizons by a relatively late episode of brittle-ductile flexural-slip movement (Horne and

Culshaw, 2001). Regional metamorphic grade is greenschist facies throughout the majority of the Meguma Terrane, though amphibolite facies rocks are present at both the western and eastern extents. Relationships between fold structures and regional metamorphism suggest that the major phase of deformation typically preceded regional metamorphism (Taylor and Schiller, 1966).

Several other rock types were introduced to the Meguma Terrane following the onset of Acadian metamorphism and deformation. These include: (1) an extensive suite of ca. 370 Ma crustally-derived, peraluminous granitoid intrusions (Clarke et al., 1997), with associated metamorphic aureoles, (2) a suite of ca. 370 Ma shoshonitic lamprophyre dykes in the eastern portion of the Meguma Zone (Clarke et al., 1997), (3) Upper Devonian – Lower Carboniferous molasse deposits, reflecting Alleghanian uplift along the Cobequid – Chedabucto Fault, and (4) Mesozoic volcanic and siliciclastic rocks filling late extensional grabens.

• Meguma Gold Deposits Geology:

The MGD occur throughout the geographic extent of the Meguma Terrane (Fig.3), but are invariably confined to Meguma Group sediments. Kontak et al. (2001) emphasize that gold mineralization in the Meguma Group is not preferential to a particular stratigraphic position or metamorphic grade, but rather is structurally-controlled. This is evident due to the proximity of Au mineralization to anticlinal fold hinges and steeply-dipping shear zones on fold limbs, which mineralizing fluids apparently utilized as transport planes during fluid migration. Two main styles of mineralization are present, separate or in combination, including disseminated and quartz vein-associated (Ryan and

Smith, 1998). Disseminated mineralization occurs in both Goldenville and Halifax Group sediments, and though not as common as vein-associated deposits, can still be economically significant (e.g. Touquoy Zone at Moose River; Ryan and Smith, 1998; see figure 3 for location). The significant gold mineralization at disseminated deposits occurs as free grains, and is associated with one or more of several alteration assemblages, including carbonate, sulfide, silica, and sericite (Ryan and Smith, 1998).

Vein-associated deposits are prevalent throughout the Meguma Terrane, and though characteristically variable on the basis of individual deposits, are generally very similar in many respects. Gold-bearing veins range in thickness from <1 cm to >5 m, and in length from <1m to >1 km. As with disseminated deposits, the presence of extensive silicification and carbonatization alteration haloes is observed adjacent to veins of vein-associated deposits. Quartz is the most common mineral constituent of the veins, but several accessory minerals, including calcite, chlorite, albite, muscovite, amphibole, tourmaline, and epidote are also present in variable amounts. Arsenopyrite is the predominant sulfide phase in the veins, in addition to variable amounts of pyrite, pyrrhotite, chalcopyrite, galena, and rare sphalerite and molybdenite. Gold mineralization occurs as fine to medium-grained native gold within quartz veins, near crack-seal laminae, along vein-wall contacts, and within fluid inclusions (Ryan and Smith, 1998). Gold distribution also commonly follows that of arsenopyrite (Graves and Zentilli, 1982), occurring as fine disseminations within, or as coatings on grain boundaries or fracture surfaces of arsenopyrite crystals (Kontak and Smith, 1993a). These textural relationships indicate derivation of gold and arsenopyrite from a common fluid source, and a very close temporal relationship between gold and arsenopyrite in the MGD. Thus,

age determination of arsenopyrite in this study results directly in the determination of the age of gold mineralization.

Several different vein-types are present at individual deposits, each reflecting a different geometry with respect to the orientation of the folded host strata. The range of vein orientations present at MGD have been described previously in considerable detail by several authors (e.g. Henderson et al., 1986; Haynes, 1987; Smith and Kontak, 1988; Williams and Hy, 1990; Horne and Culshaw, 2001), but can be generally grouped into one of three categories: (a) bedding-parallel (-concordant), (b) saddle-reef, or (c) bedding-discordant veins. For this study, the most recent vein classification (Horne and Culshaw, 2001) is adopted with the exception that saddle-reef veins are treated separately from bedding-parallel veins, such that bedding-parallel veins include any vein with an orientation parallel or nearly parallel to that of bedding, whereas saddle-reef veins comprise only those veins that are situated within the hinge of an anticline, are thickest in the axial zone, and have an orientation parallel to bedding. Bedding-discordant veins include all remaining vein geometries, and are characterized by their orientation at a high angle with respect to bedding.

It was initially hypothesized that all vein-associated gold mineralization in the Meguma Terrane was invariably concentrated within saddle-reef structures (Faribault, 1899). However, subsequent work has shown that, in fact, true saddle-reef veins are uncommon among MGD, and that gold mineralization, though most commonly present in bedding-concordant veins, can exist in all vein types (Kontak et al., 1991). However, the timing of vein emplacement and genesis of different vein-types is a highly contentious

issue, with diverse interpretations proposed by numerous workers (see Table 1 for summary of models). In this study, the timing of vein emplacement and associated gold mineralization is resolved through use of Re-Os geochronology of arsenopyrite. In order to perform a comprehensive evaluation of the relative vein ages, two deposits that, together, exhibit all three vein geometries were the focus of a detailed Re-Os geochronology study. These two deposits, The Ovens and Dufferin, are briefly described as follows:

i) The Ovens:

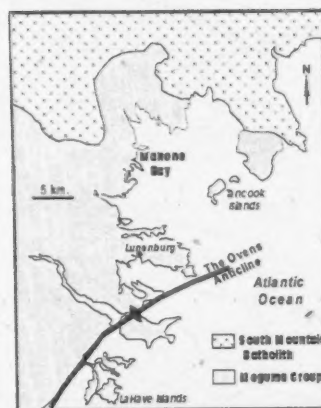
This deposit is located on the coast of southwestern Nova Scotia near Lunenburg (Fig.4), and is hosted by greenschist facies slate and subordinate metasandstone interbeds of the Lower Halifax Formation. The South Mountain Batholith, located ~ 25 km. to the north, is the nearest intrusive body to the Ovens deposit. The major structural feature present is the Ovens Anticline, a tight, steeply inclined, northeasterly (gently) plunging chevron fold, with planar limbs, numerous bedding-parallel movement horizons related to flexural slip, and with several small thrust faulted blocks adjacent to the southeastern limb (Horne and Culshaw, 2001). Representatives of all vein geometries are present at this deposit. The Ovens was previously the subject of detailed metamorphic (Hicks et al., 1999) and structural (Horne and Culshaw, 2001) investigations.

Table 1: Summary of recent models proposed for MGD formation.

Model (proponents):	Host Au mineralization:	Timing:	*Relative vein ages:	Source:
Syngenetic (Haynes, 1987).	bedding-parallel veins	pre-tectonic	BP = very early, BD = late	hydrothermal, seafloor
Lateral Secretion (Boyle, 1966; McBride, 1978).	bedding-parallel veins	early syntectonic, pre-folding	BP = early, BD = late	Meguma Group
Hydraulic Fracturing / 'Crack-Seal' + Lateral Secretion (Graves and Zentilli, 1982; Henderson et al., 1986, 1990; Henderson and Henderson, 1990; Sangster, 1990).	bedding-parallel veins	early syntectonic, pre-folding	BP = early, BD = late	Meguma Group
Saddle-Reef (Keppie, 1976; Mawer, 1986, 1987).	saddle reef veins	late syntectonic	Saddle-reef only vein-type considered.	metamorphic fluids
Thermal Doming (Hy, 1986; Williams and Hy, 1990).	bedding-parallel veins	late syntectonic (synintrusion)	BP = early (though not pre-folding), saddle + BD (undeformed) = later	metamorphic fluids
Integrated (Kontak and Smith, 1989, 1993b; Kontak et al., 1990a, b, 1991, 1993; Kontak and Kerrich, 1995).	all vein types	late syntectonic	Simultaneous emplacement of all vein types.	Metamorphic fluids
Flexural-slip (Horne and Culshaw, 2001).	all vein types	late syntectonic	Simultaneous emplacement of all vein types.	metamorphic fluids

*BP = bedding parallel veins
BD = bedding discordant veins

Figure 4: Detailed location map of The Ovens deposit (after Hicks et al., 1999). Gold-bearing veins are located in close proximity to the Ovens Anticline.



ii) Dufferin:

The Dufferin deposit is located approximately 100 km. northeast of Halifax (Fig.3), and reserves at the deposit are estimated to be 103 000 t at 13 g/t Au (Duncan, 1993). This deposit is hosted by greenschist facies Goldenville Group metasandstone or silty metasandstone with minor interbeds of slate, and mineralized veins are situated within a satellitic anticlinal structure located on the limb of a larger fold. This deposit is one of few MGD considered to be a true saddle-reef deposit, as mineralization occurs within and adjacent to stratabound, stacked veins in the crest of the anticline (Fig. 5). The veins are assymetric, are thickest in the hinge region (>6m), and thin considerably down the limbs of the fold (<30 cm) (Ryan and Smith, 1998).

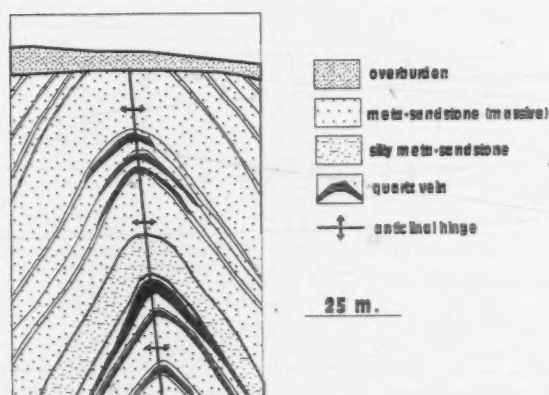


Figure 5: Detailed cross-section, looking ENE through the Dufferin deposit (after Ryan and Smith, 1998).

Chapter 3 – Sampling and Analytical Methods:

Red Dog sulfide samples analyzed for this study are listed in Table 2. The samples were petrogenetically characterized by their relationship to specific “types” or stages of sphalerite, which are delineated by their color and trace element chemistry (Kelley et al., 2004). Main stage ore at Red Dog comprises two sphalerite stages: stage 2 yellow to reddish-brown sphalerite (YBS) and stage 3 coarse-grained, strongly zoned red-brown sphalerite (RBS).

All pyrite mineral separates, except for VP950, were produced by rough crushing and subsequent hand-picking of pyrite grains. Separates of sample VP950 and all sphalerite samples were obtained by drilling mineral grains into a very fine-grained powder with a Dremel diamond-tipped drill. XRD analyses were performed on all samples to ensure sample purity, and revealed that most pyrite samples contain only traces of marcasite, and that sphalerite samples SS136 and SS139 contain small proportions of galena. Neither contaminant was considered problematic for determining Re-Os isotopic abundances as petrogenetic studies indicate that the marcasite and galena precipitated from the same hydrothermal fluids as the pyrite and sphalerite, respectively (K.D. Kelley, pers. comm.).

All MGD samples analyzed in this study were collected in-situ by the author during a short field campaign in 2002. Sample descriptions and characteristics of MGD samples are summarized in Table 3. As with the Red Dog samples, XRD analyses were performed on representative samples, and no impurities were identified in any sample.

Table 2: Petrogenetic relationships/locations of Red Dog samples used for Re-Os isotopic analysis.

Sample	Mineral:	Paragenetic stage: ¹	Location: ²
MP9001	pyrite	intergrown with stage 2 sphalerite	southern portion of Main deposit
MS136	sphalerite	stage 2 sphalerite	drillhole 492 @ 136.5'
MS139	sphalerite	stage 2 sphalerite	drillhole 954 @ 139' (Qanaiyaq)
VS950	sphalerite	stage 3 sphalerite	southern portion of Main deposit
VP950	pyrite	associated with stage 3 sphalerite	southern portion of Main deposit
VP4	pyrite	associated with stage 3 sphalerite	southern portion of Main deposit
VP5	pyrite	associated with stage 3 sphalerite	southern portion of Main deposit

¹paragenetic stages used as described by Kelley et al., 2004.

²refer to Figure 1. Descriptions indicate location of surface exposure, unless stated as drillhole.

Table 3: Descriptions of samples used for Re-Os analysis from Meguma Gold Deposits.

Deposit:	Sample no.:	Vein Type:	Sample Description:	Figure:
Ovens:	OV3c	Bedding-Parallel	Crushed portions of several small crystals picked from one vein.	n/a
	OV6a,d	Bedding-Parallel	Crushed, separate portions from mixture of two large crystals picked from one vein.	6b
	Ov5a,b	Bedding-Discordant	Crushed, separate portions of single large crystal from vein cutting NW limb of Ovens anticline.	6a
Dufferin:	D4a	Saddle Reef (massive)	Drilled from single crystal from Saddle #1 (i.e. uppermost saddle; Fig.5).	6c
	D4b	Saddle Reef (massive)	Drilled from single crystal from Saddle #1 (different crystal than D4a).	6c
	D6	Saddle Reef (massive)	Drilled from single crystal from Saddle #2 (i.e. 2nd saddle below surface; Fig.5).	n/a

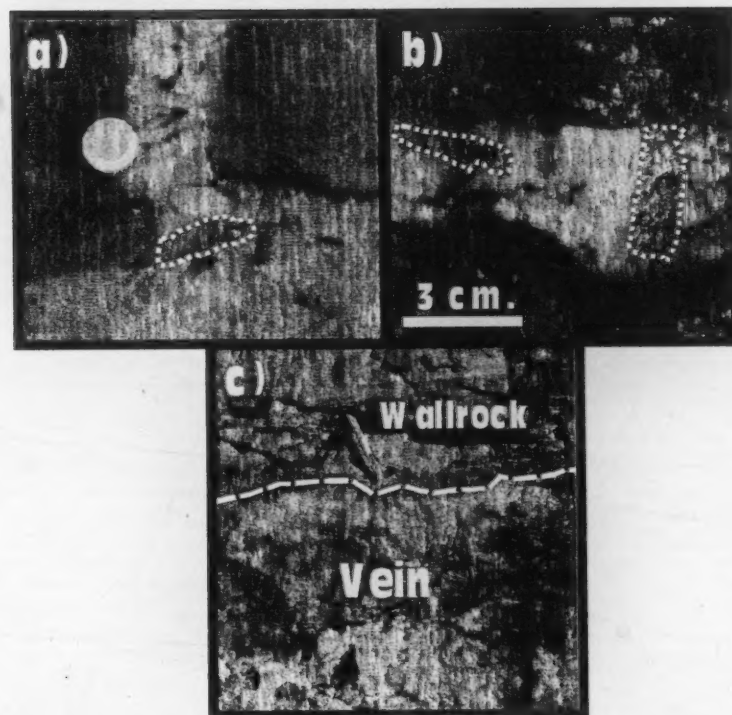


Figure 6: Photographs of (a) arsenopyrite crystal (sample OV5) in bedding-discordant vein at The Ovens, (b) 2 arsenopyrite crystals in bedding-concordant quartz vein (both crystals = sample OV6) at The Ovens, and (c) saddle reef quartz vein #1 at Dufferin, from which sample D4 is derived (hammer for scale ~45 cm. long).

Analyses were performed according to the procedure described by Selby and Creaser (2001a, b) and Creaser et al. (2002), with modifications. Sample fractions were weighed with a known amount of mixed $^{185}\text{Re} + ^{190}\text{Os}$ spike and digested by the Carius tube method. A maximum of 200 mg of sample was used for pyrite in order to inhibit potential effects of the Claus process, which results in the preferential oxidation of H_2S to S over Os to OsO_4 during sample dissolution (Frei et al., 1998). However, a 500 mg sample was used for one arsenopyrite analysis (D4a-2) as a test to determine if larger sample sizes can be used, as no studies have previously evaluated the effects of the Claus process on Re-Os analyses of arsenopyrite. Sphalerite sample sizes ranged from

approximately 200 to 500 mg, based on the assumption that the Claus process would not be a consequence of larger sphalerite samples sizes, due to a smaller proportion of Fe relative to pyrite. The tubes were sealed following the addition of 4.5ml to 12ml of inverse aqua regia (i.e. 2:1 ratio of 16N HNO₃ : 12N HCl), and were heated at 240°C for ~24 hours to ensure complete sample dissolution and sample-spike equilibration (Shirey and Walker, 1995). Re and Os fractions were subsequently separated through a modified solvent extraction procedure utilizing carbon tetrachloride (CCl₄) (Cohen and Waters, 1996; Pearson and Woodland, 2000). Re was further purified through anion-exchange chromatography, while Os was purified through a modified microdistillation procedure (Birck et al., 1997). MGD Re fractions were purified using a single DOWEX AGI-X8 anion exchange resin bead (<20 mesh) technique in order to overcome poor beam signals during mass spectrometry, possibly due to As interference.

Following separation and purification of Re and Os fractions, Re and Os contents were determined via isotope dilution negative thermal ionization mass spectrometry (Creaser et al., 1991; Völkening et al., 1991) on a Micromass Sector 54 mass spectrometer at the University of Alberta Radiogenic Isotope Facility. Dried Re cuts were dissolved in ~1 µl 16N HNO₃, loaded onto an outgassed Ni wire filament, and were coated with ~0.4 µl Ba(NO₃)₂ activator. Dried Os fractions were dissolved in ~0.5 µl 9N HBr and loaded, along with a thin coating of Ba(OH)₂/NaOH activator, onto a fluxed Pt ribbon filament. All Re analyses and one Os analysis (900-1-2) were measured by static Faraday collector analysis, while the remaining Os analyses were performed using an ETP electron multiplier detector in pulse counting mode. Procedural blanks were monitored and cover the range of reagent volumes used for sample dissolution. For Red

Dog, total Re blanks ranged from 1.7 - 5.3 pg, while Os blanks ranged from 0.7-3.0 pg and have an average $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.52 ± 0.3 (n=6). For the MGD, total Re blanks ranged from 0.7-3.0 pg, whereas Os blanks ranged from 0.7 - 1.5 pg with $^{187}\text{Os}/^{188}\text{Os}$ ratios ranging from 0.167 - 0.300 (n=5). Isochron ages were calculated using Isoplot/Ex (Ludwig, 2000), using an uncertainty of 1% (2σ) for $^{187}\text{Re}/^{188}\text{Os}$ and the measured value of $2\sigma_m$ for $^{187}\text{Os}/^{188}\text{Os}$ ratios.

Chapter 4 – Results:

a) Red Dog:

In total, 19 Re-Os isotopic analyses were obtained, including 10 from 4 pyrite samples and 9 from 3 sphalerite samples (Table 4). This selection of samples represents both massive sulfide ore (3 pyrite and 7 sphalerite analyses), and vein ore (7 pyrite and 2 sphalerite).

Previous studies (Stein et al, 1998a; Mathur et al., 1999) indicate that the Re-Os isotopic system in pyrite may be disturbed in settings subject to extensive metamorphism and/or metasomatism subsequent to mineral crystallization. However, other studies (Brenan et al., 2000; Stein et al., 2000) suggest that, in regions unaffected by later extensive metamorphic or hydrothermal activity, pyrite can yield reliable Re-Os ages. Consequently, age determination of Red Dog ore was initially approached using pyrite, as rocks in the Red Dog region are unmetamorphosed (Dusel-Bacon, 1994), and hydrothermal fluids did not exceed temperatures of $\sim 200^\circ\text{C}$ during ore formation (Young, 1989; Leach et al., 2004).

Seven Re-Os analyses of pyrite from vein ore show a limited range in Re ($\sim 15 - 31$ ppb) and Os ($\sim 0.1 - 0.2$ ppb) abundances, but a much larger range in $^{187}\text{Re}/^{187}\text{Os}$

(~387 – 5020), and Os isotopic composition (Table 4), with ^{187}Os comprising ~24 to 80% of all Os in these samples. All seven analyses define a Model 3 errorchron age of 337.4 ± 8.7 Ma (Fig. 7; MSWD = 8.2, 2σ). The three analyses of pyrite from massive ore contain significantly more Re (351 – 383 ppb) and Os (3.3 – 3.6 ppb) than the vein pyrite, but due to a very small range in $^{187}\text{Re}/^{187}\text{Os}$ (800 – 805) and Os isotopic compositions, cannot be regressed separately. However, it is clear that these analyses fall very close to the regression line defined by the vein pyrite samples (Fig. 8), and if regressed together, the ten analyses of vein plus massive pyrite yield an indistinguishable Model 3 age of 338.3 ± 5.8 Ma (MSWD = 7.8, 2σ). It is here suggested that this date, comprising both massive sulfide ore and cross-cutting vein ore, best represents the age of main stage ore mineralization at Red Dog.

Sphalerite and pyrite in massive sulfide ore are texturally intergrown and assumed to have formed contemporaneously and in equilibrium (Edgerton, 1997; Kelley et al., 2004). In vein ore, sphalerite and pyrite are also cogenetic, as they exist as alternating colloform bands. Seven Re-Os analyses of sphalerite from massive ore and two from vein ore show a more limited range in Re (~0.7 – 11.2 ppb) and Os (~0.01 – 0.15 ppb) abundances, $^{187}\text{Re}/^{187}\text{Os}$ (~167 – 568), and Os isotopic composition (Table 4) than pyrite analyses, and ^{187}Os comprises ~14 to 33% of Os in these samples. Regression of the Re-Os data for all nine sphalerite analyses (Fig. 9) yields an imprecise age of 416 ± 75 Ma, with a large degree of scatter about the regression line (MSWD = 418). Neither the age uncertainty nor the degree of scatter improve significantly by considering only samples with ≥ 200 mg sample weights (422 ± 30 Ma, MSWD = 16), indicating that non-equilibration of sample and spike Os relating to sample weight is likely not a cause for

this scatter. The sphalerite Re-Os analyses are shown relative to the 338 Ma pyrite regression in Figure 10. Some samples do plot close to this regression line, such as sphalerite sample MS136 from massive sulfide ore. Analyses from another sample of sphalerite from massive sulfide ore (MS139) plot well above the pyrite regression, whereas a sphalerite sample from vein ore (VS950) plots below.

Table 4: Re-Os isotope data for sulfide minerals from Red Dog.

Sample	Mineral	Ore Facies	Sample wt. (g)	Total Re (ppb)	Total Os (ppb)	$^{187}\text{Re}/^{188}\text{Os}$	$^{187}\text{Os}/^{188}\text{Os}^1$	^{187}Os (ppb)	$^{187}\text{Os}/\text{Total Os}$ (%)
MP9001-2	Pyrite	Massive	0.212	351	3.353	799.6	4.657 ± .002	1.280	38.2
MP9001-3	Pyrite	Massive	0.108	383	3.637	805.2	4.726 ± .023	1.409	38.7
MP9001-4	Pyrite	Massive	0.199	382	3.620	805.5	4.686 ± .023	1.391	38.4
VP4-1	Pyrite	Vein	0.108	24.8	0.108	3543	19.76 ± .107	0.0865	80
VP4-2	Pyrite	Vein	0.154	31.4	0.141	5021	28.63 ± .113	0.112	79.4
VP4-3	Pyrite	Vein	0.160	24.3	0.116	4047	23.32 ± .143	0.0877	75.6
VP5-1	Pyrite	Vein	0.107	17.6	0.138	989	5.884 ± .193	0.0654	47.5
VP5-2	Pyrite	Vein	0.151	17.0	0.098	2257	13.18 ± .080	0.0627	63.9
VP950-1	Pyrite	Vein	0.184	14.7	0.235	387.3	2.384 ± .013	0.0565	24
VP950-2	Pyrite	Vein	0.170	15.3	0.201	507.1	3.134 ± .018	0.0592	29.4
MS136-1	Sphalerite	Massive	0.507	4.97	0.105	278.4	1.834 ± .007	0.105	19.6
MS136-3	Sphalerite	Massive	0.193	3.94	0.13	166.7	1.212 ± .018	0.0170	13.9
MS136-4	Sphalerite	Massive	0.199	3.86	0.117	180.6	1.238 ± .005	0.0170	14.1
MS139-1	Sphalerite	Massive	0.509	10.7	0.137	544.2	3.612 ± .007	0.0440	32.4
MS139-2	Sphalerite	Massive	0.517	10.8	0.134	568.3	3.633 ± .004	0.0430	32.5
MS139-3	Sphalerite	Massive	0.198	11.2	0.152	514.9	3.627 ± .006	0.0490	32.5
MS139-4	Sphalerite	Massive	0.201	10.7	0.149	496.4	3.506 ± .010	0.0470	31.7
VS950-1	Sphalerite	Vein	0.517	0.682	0.012	319.1	1.690 ± .005	0.0020	18.3
VS950-2	Sphalerite	Vein	0.507	0.644	0.014	257.5	1.331 ± .014	0.0020	14.9

¹ results are blank-corrected (0.7-3.0 pg, $^{187}\text{Os}/^{188}\text{Os}=0.52 \pm 0.3$) and uncertainty reported as $2\sigma_m$.

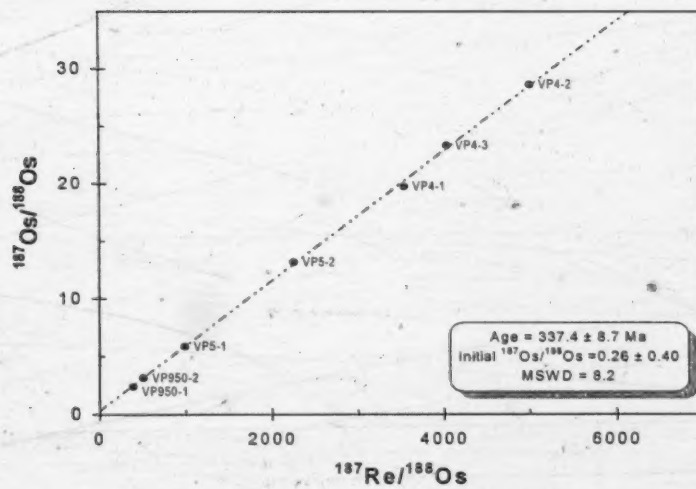


Figure 7: Re-Os isochron diagram for vein pyrite samples from Red Dog deposit.

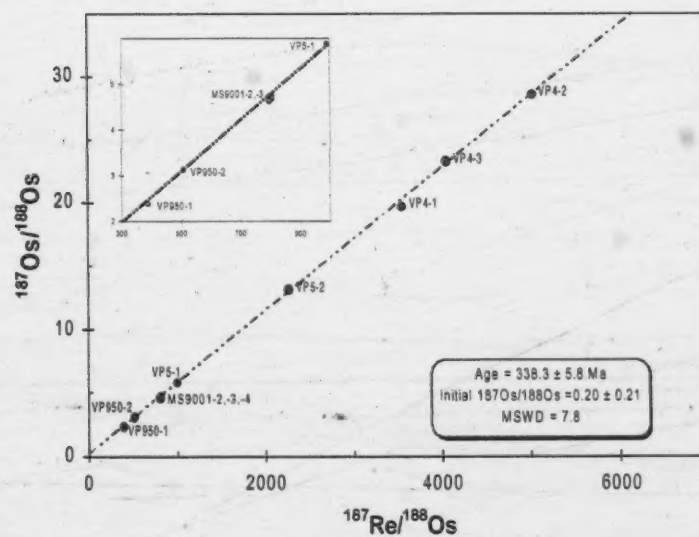


Figure 8: Re-Os isochron diagram showing both massive and vein ore pyrite samples.

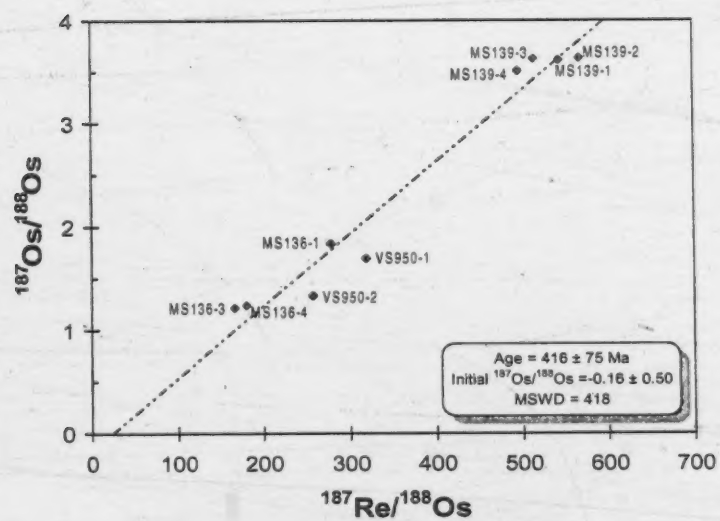


Figure 9: Re-Os isochron diagram showing both massive and vein ore sphalerite samples.

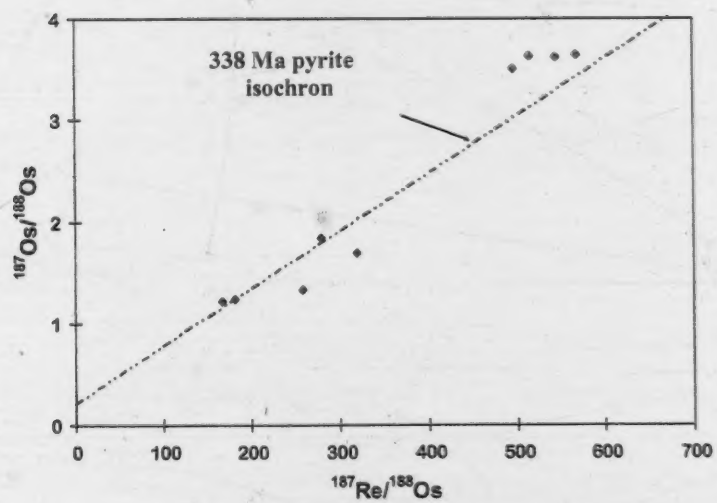


Figure 10: Re-Os isochron diagram showing sphalerite Re-Os analyses relative to the 338 Ma pyrite Re-Os isochron for Red Dog main stage ore.

b) Meguma Gold Deposits:

A total of 14 Re-Os analyses were performed on MGD arsenopyrite, including 7 analyses from The Ovens and 7 analyses from Dufferin. Of these analyses, 4 are from bedding-parallel vein arsenopyrite (OV3 and OV6) and 3 are from discordant conjugate vein arsenopyrite (OV5) from The Ovens, whereas all 7 analyses of Dufferin samples are from saddle-reef vein arsenopyrite. In order to delineate the relative timing of vein emplacement, all vein types are initially evaluated separately.

The Re-Os results for all MGD analyses are reported in Table 5. For analyses from The Ovens deposit, total Re and Os abundances for all vein types are very consistent, though much larger differences are observed for the Re-Os isotopic compositions between different samples. Analyses of the Dufferin deposit sulfides are very similar to those from The Ovens in that they exhibit a limited range of total Re (1.3 – 6.8 ppb) and Os (0.013 – 0.029 ppb) concentrations, but a wide range in Re-Os isotopic compositions.

Due to extremely high $^{187}\text{Re}/^{188}\text{Os}$ ratios for some of the MGD arsenopyrite, data regression was carried out in a manner different than that used for Red Dog samples, and was performed using the parameters suggested by Stein et al. (2000) for work with LLHR (low-level highly-radiogenic) samples. Whereas regressions of all samples yielding $^{187}\text{Re}/^{188}\text{Os}$ ratios <5000 were performed using a standard $^{187}\text{Re}/^{188}\text{Os}$ vs. $^{187}\text{Os}/^{188}\text{Os}$ plot, those samples yielding ratios >5000 were evaluated on a ^{187}Re vs. ^{188}Os plot so as to avoid highly correlated errors derived from large uncertainties in the measurement of very small amounts of ^{188}Os . For regressions including analyses with $^{187}\text{Re}/^{188}\text{Os}$ both below and above 5000, both types of plots are compared. An additional function, rho (see

Appendix 1), is used for all analyses used for $^{187}\text{Re}/^{188}\text{Os}$ vs. $^{187}\text{Os}/^{188}\text{Os}$ regressions, and quantifies the correlation between errors in the ^{188}Os measurement in both the x and y axes. Reported age uncertainties for all regressions and single-mineral model ages do not include sample and spike weighing uncertainties due to the use of a mixed Re-Os spike (i.e. the weighing error is equivalent for both elements, and can therefore be ignored).

Table 5: Re-Os isotope data for MGD arsenopyrite.

Sample no.	Sample wt. (g)	Reagent Vol.	Total Re (ppb)	^{187}Re (ppb)	^{192}Os (ppt)	$^{187}\text{Re}/^{188}\text{Os}$	$^{187}\text{Os}/^{188}\text{Os}^1$	Rho:	^{187}Os (ppt)	$^{187}\text{Os}/\text{Total Os}$ (%)	Model Age ² (Ma)
OV3c-1	0.200	6ml : 3ml	7.2	4.5	3.0	4816	33.80 ± 9.12	1.000	32	82	409.9 ± 6.2
OV3c-2	0.209	6ml : 3ml	7.4	4.7	3.9	3807	26.62 ± 8.00	0.999	33	79	405.7 ± 8.3
OV6a-5	0.201	6ml : 3ml	2.6	1.7	8.6	614.6	4.947 ± 0.701	0.988	13	38	404 ± 41
OV6d-1	0.206	6ml : 3ml	2.9	1.8	3.6	1560	11.70 ± 3.777	0.999	13	59	417 ± 19
OV5a-2	0.204	6ml : 3ml	7.2	4.5	1.4	10062	68.76 ± 57.18	1.000	31	91	404.1 ± 7.7
OV5b-1	0.203	6ml : 3ml	8.6	5.4	0.1	277582	1900 ± 12410	1.000	37	100	409.2 ± 6.8
D6-1	0.201	6ml : 3ml	1.6	1.0	4.1	767.5	5.259 ± 1.041	0.990	7	44	348 ± 35
D6-2	0.201	6ml : 3ml	1.2	0.8	3.1	792.3	5.415 ± 1.388	0.991	5	38	349 ± 36
D4a-1	0.200	6ml : 3ml	6.5	4.1	1.3	9939	63.69 ± 20.01	0.999	26	90	378.6 ± 5.4
D4a-2	0.513	9ml : 3ml	6.0	3.8	0.1	88048	561.6 ± 1980	1.000	24	100	381.1 ± 5.0
D4b-1	0.198	6ml : 3ml	6.0	3.8	1.6	7583	48.51 ± 25.10	1.000	24	86	376.5 ± 6.3
D4b-2	0.198	6ml : 3ml	5.7	3.6	1.0	11667	74.87 ± 62.62	1.000	23	92	379.9 ± 5.8

¹results are blank corrected (0.7-1.5 pg, $^{187}\text{Os}/^{188}\text{Os}=0.167-300$);
²uncertainties reported as $2\sigma_m$.

² 2σ uncertainties.

Table 6: Re-Os isotope data for MGD arsenopyrite used for calculation of fractionation-corrected model ages.

Sample no.	Deposit	Sample wt. (g)	Reagent Vol. (HNO ₃ : HCl)	Total Re (ppb)	^{187}Re (ppb)	^{187}Os (ppb)	Model Age (Ma)
OV5b-2	The Ovens	0.208	6ml : 3ml	5.4	3.4	0.036	406.9 ± 1.7
D4a-3	Dufferin	0.201	6ml : 3ml	6.8	4.3	0.027	380.6 ± 1.5

Regression of the 4 analyses from bedding-parallel vein sulfides, characterized by $^{187}\text{Re}/^{188}\text{Os}$ ratios ranging from ~600 to ~5000, yields a Model 1 isochron age of 408.6 ± 4.5 Ma (Fig. 11; MSWD = 1.8, 2σ). Two analyses from bedding-discordant vein sulfides (OV5a-2, OV5b-1) had considerably higher $^{187}\text{Re}/^{188}\text{Os}$ ratios (~10,000 and 275,000, respectively), such that the contribution of common ^{187}Os to the total ^{187}Os in each sample is negligible. Therefore, an isochron approach to age determination is abandoned, and a single mineral model age is calculated for these samples. Model ages for discordant as well as bedding-parallel arsenopyrite are listed in Table 5, and are calculated assuming an initial Os isotopic composition of 0.82 ± 0.16 , as derived from a $^{187}\text{Re}/^{188}\text{Os}$ vs. $^{187}\text{Os}/^{188}\text{Os}$ regression of combined bedding-parallel and -discordant analyses (Fig. 12). The assumed initial Os composition used has less of an influence on model ages with higher $^{187}\text{Re}/^{188}\text{Os}$ (i.e. with less initial Os), and thus the model ages calculated for the discordant samples should be the most accurate, assuming there has been no post-crystallization redistribution of Re and/or Os. Model ages for the discordant samples are 404.1 ± 7.7 Ma and 409.2 ± 6.8 Ma (2σ). These ages are identical to the age of the bedding-parallel vein sulfides, within associated uncertainty, thereby suggesting a contemporaneous relationship for both bedding-parallel and -discordant veins.

As an independent check on the accuracy of the model ages, a single analysis of the sample with the highest $^{187}\text{Re}/^{188}\text{Os}$ ratio (OV5b; $^{187}\text{Re}/^{188}\text{Os} > 275,000$) was performed using a mixed ^{185}Re and isotopically normal Os spike. This methodology is essentially 'reverse' isotope dilution, in that the ^{187}Os in the sample, assumed to be devoid of common ^{187}Os , acts as the 'spike' isotope. This is identical to the technique used by Selby and Creaser (2001) for molybdenite, and is advantageous to a mixed single

Re/Os isotope spike method because precise Os isotope mass fractionation corrections can be made. For sample OV5b, this method yielded a Re-Os model age of 406.9 ± 1.6 Ma (Table 6), which compares extremely well with all of the isochron age of bedding-parallel vein arsenopyrite (408.6 ± 4.5 Ma), the model ages from discordant veins (404.1 ± 7.7 Ma and 409.2 ± 6.8 Ma), and $^{187}\text{Re}/^{188}\text{Os}$ vs. $^{187}\text{Os}/^{188}\text{Os}$ (407 ± 4.1 Ma; Fig. 12; MSWD = 1.6, 2σ) and ^{187}Re vs. ^{188}Os (404 ± 12 Ma; Fig. 13; MSWD = 0.58, 2σ) Model 1 isochron ages from regressions of discordant plus bedding-parallel arsenopyrite analyses (see Fig. 14). These ages are here interpreted to indicate the simultaneous formation of all vein-associated mineralization (including Au) at The Ovens deposit at 406.9 Ma.

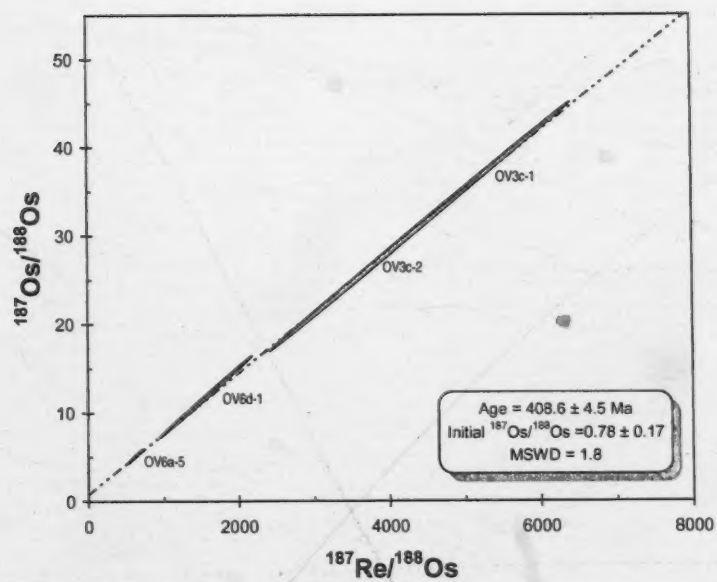


Figure 11: $^{187}\text{Re}/^{188}\text{Os}$ vs. $^{187}\text{Os}/^{188}\text{Os}$ isochron diagram showing arsenopyrite Re-Os analyses from bedding-concordant veins at The Ovens.

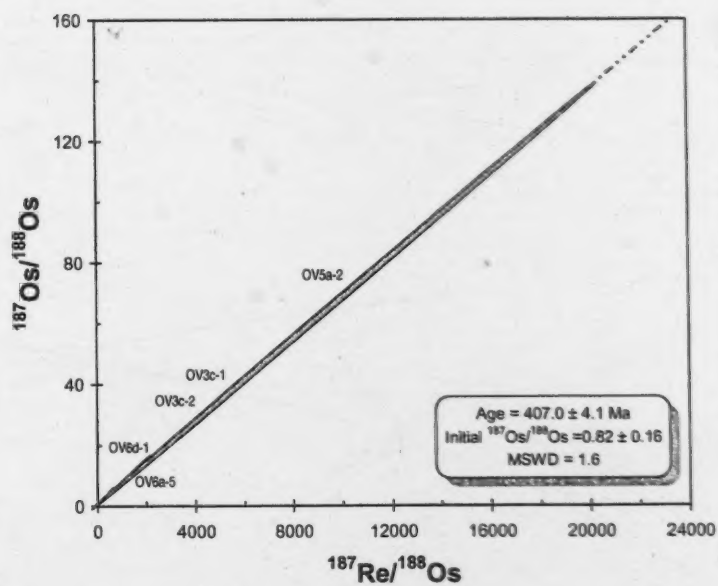


Figure 12: $^{187}\text{Re}/^{188}\text{Os}$ vs. $^{187}\text{Re}/^{188}\text{Os}$ isochron diagram showing arsenopyrite Re-Os analyses (excluding OV5b-1) from all vein-types at The Ovens. Large error ellipses arise from very highly correlated errors resulting from imprecise ^{188}Os measurements for samples with high Re/Os ratios (e.g. OV5a,-b).

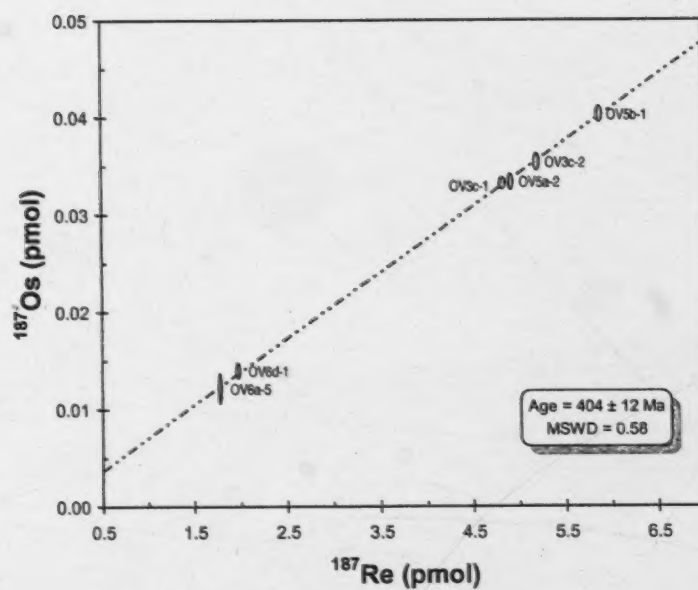


Figure 13: ^{187}Re vs. ^{187}Os isochron diagram showing arsenopyrite Re-Os analyses of all vein types at The Ovens.

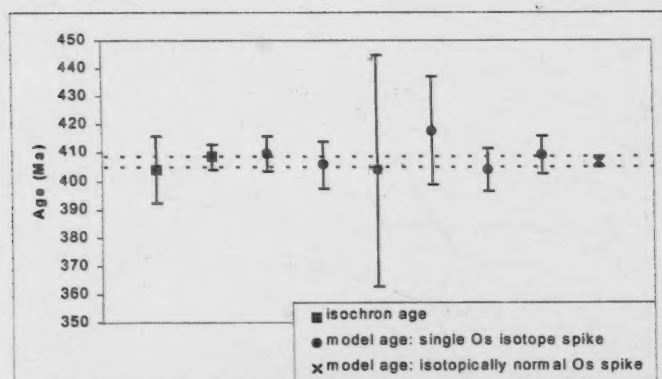


Figure 14: Comparison of all Re-Os ages determined in this study for The Ovens deposit.

All arsenopyrite samples from Dufferin are derived from saddle reef veins and are therefore regressed collectively, despite highly variable $^{187}\text{Re}/^{188}\text{Os}$ for different samples. A $^{187}\text{Re}/^{188}\text{Os}$ vs. $^{187}\text{Os}/^{188}\text{Os}$ plot yields an extremely precise isochron age of 381.0 ± 3.3 Ma (Fig. 15; MSWD = 0.13), whereas a ^{187}Re vs. ^{188}Os regression yields a slightly less precise, though identical, isochron age of 381.3 ± 5.3 Ma (Fig. 16; MSWD=0.08). Model ages were calculated for all samples (Table 5) assuming an initial Os isotopic composition of 0.37 ± 0.14 , identical to that determined with the $^{187}\text{Re}/^{188}\text{Os}$ vs. $^{187}\text{Os}/^{188}\text{Os}$ regression (Fig. 15). All model ages cluster around ~381 Ma, and are within 2σ uncertainties of the isochron ages for the Dufferin analyses.

As with sample OV5b from The Ovens, an additional analysis of Dufferin sample D4-a was performed using an isotopically normal Os spike to allow for Os isotope fractionation corrections, and as an independent check on the accuracy of the age. This analysis (D4a-3), the results of which are reported in Table 6, yielded a Re-Os model age of $380.6 \text{ Ma} \pm 1.6 \text{ Ma}$. This age is identical to all isochron and model ages calculated for Dufferin (see Fig. 17), and is here interpreted to represent the age of emplacement of

saddle reef veins as well as cogenetic arsenopyrite and Au mineralization at the Dufferin deposit.

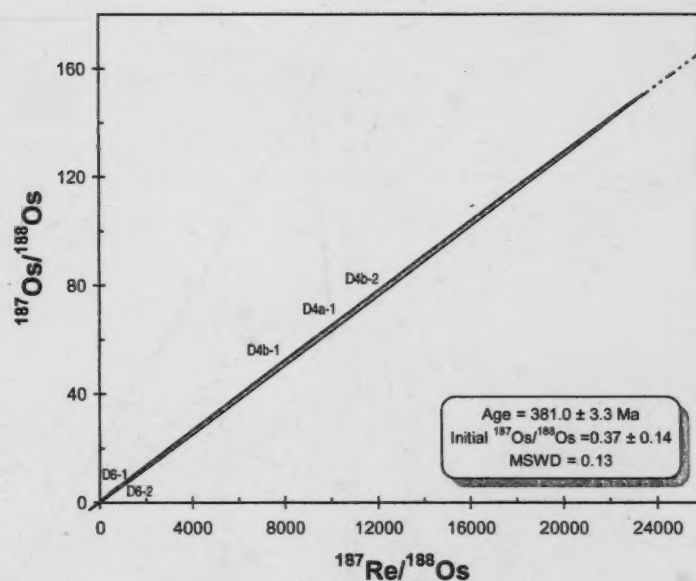


Figure 15: $^{187}\text{Re}/^{188}\text{Os}$ vs. $^{187}\text{Os}/^{188}\text{Os}$ isochron diagram showing arsenopyrite Re-Os analyses of samples from #1 and #2 saddle reef veins (excluding D4a-2) at the Dufferin deposit.

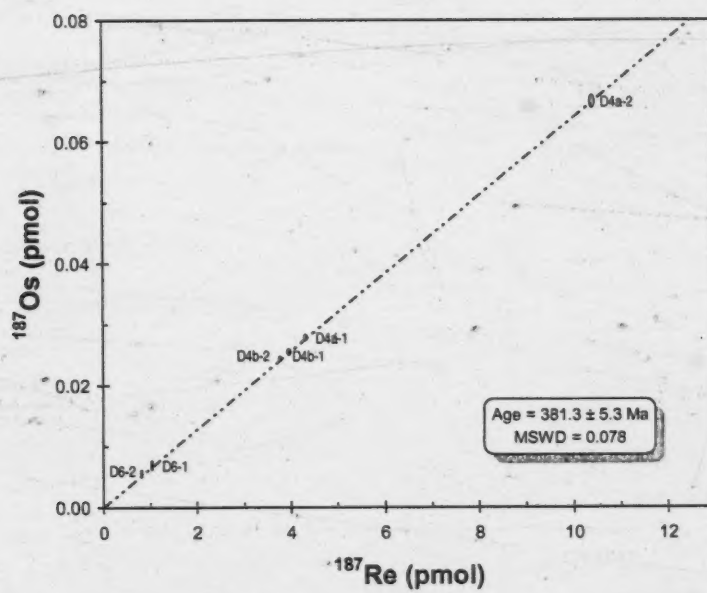


Figure 16: ^{187}Re vs. ^{187}Os isochron diagram showing arsenopyrite Re-Os analyses of samples from #1 and #2 saddle reef veins at the Dufferin deposit.

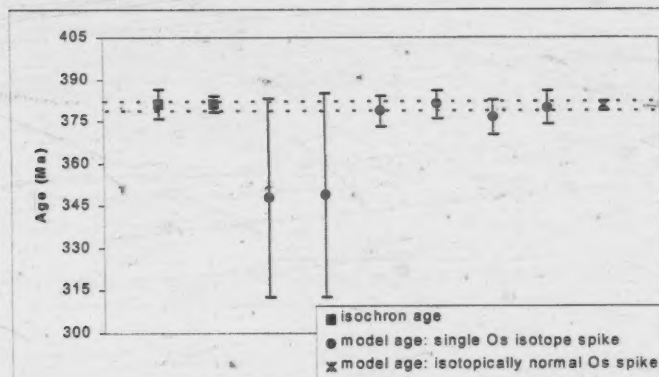


Figure 17: Comparison of all Re-Os ages determined in this study for the Dufferin deposit.

Chapter 5 - Discussion

a) Red Dog:

Age Constraints:

A combination of biostratigraphic, textural, and isotopic data provide the existing age constraints for main stage ore mineralization at Red Dog, against which the Re-Os data can be compared. Conodont and radiolarian biostratigraphy indicates that the upper Ikalukrok unit, host of all main stage mineralization, has an age range of Meramecian to early Chesterian (Dumoulin et al., 2004) (ca. 334 ± 4 to 327 ± 6 Ma; Okulitch, 2003). These biostratigraphic age constraints are supported by several $^{40}\text{Ar}/^{39}\text{Ar}$ mica ages from igneous rocks located in the vicinity of the Red Dog deposit and nearby Drenchwater deposit (Werdon et al., 1997) (see figure 1 for location). The maximum mineralization age at Red Dog is constrained by a 344 ± 3 Ma $^{40}\text{Ar}/^{39}\text{Ar}$ biotite age from alkaline hypabyssal mafic igneous rocks north of the Main deposit (Werdon et al., 1997). These rocks are temporally associated with volcanic tuffs and breccias near Drenchwater that

are cut by (and thus predate) sulfide mineralization (Werdon, 1997). Biotite from the volcanic tuffs and other small intrusions at the Drenchwater deposit yield $^{40}\text{Ar}/^{39}\text{Ar}$ plateau ages of ca. 337 Ma. Though this age is interpreted to represent the maximum age of mineralization at this deposit, the results of Re-Os sulfide geochronology may suggest that this particular biotite chronometer may have been reset by the ore-forming fluids, due to its close proximity to sulfide mineralization. White mica from a thin igneous sill that intrudes Ikalukrok shale from the south side of the main Red Dog deposit yields an age of ca. 314 Ma, interpreted to be a minimum age for mineralization based on textural relationships between the sill, shale, and main stage ore (Werdon et al., 1997).

Comparison of the Re-Os age of 338.3 ± 5.8 Ma determined here to these other age constraints for ore mineralization (Fig.18) verifies the accuracy of the results, as the age determined in this study overlaps (within uncertainty with the biostratigraphic data, and falls within the bounds for the mineralization constraints defined by the $^{40}\text{Ar}/^{39}\text{Ar}$ data. The observation that massive ore pyrite falls on the isochron defined by vein pyrite suggests that both ore facies were formed from the same fluid(s) and were contemporaneous within the resolution of the Re-Os isochron technique, despite their cross-cutting textural relationship. Thus, they are interpreted to be part of the same ore-forming system. Kelley et al. (2004) came to a similar conclusion based on compositional variations of sphalerite from massive and vein ore.

In addition to demonstrating a close temporal relationship between the massive and vein ore mineralization, the Re-Os age of main stage ore also allows this event to be placed within the regional geological context. The stratabound nature of some ore present at Red Dog suggests that the sulfide Re-Os age should also provide the absolute

age of sediment deposition in the stratigraphic sequence, thus suggesting that dating of sedimentary-hosted base metal deposits with demonstrable synsedimentary features is useful for chronostratigraphy. Additionally, much of the Devonian to Mississippian stratigraphy of northwestern Alaska is hypothesized to have been deposited in a basin formed as a result of a failed continental rift (Metz et al., 1981; Young, 2004). This theory is corroborated by the occurrence of several Carboniferous hydrothermal base metal deposits, such as Red Dog, in the northern Brooks Range, and Mississippian age within-plate igneous rocks of within-plate, extensively alkaline chemistry (Werdon, 1996). The evidence for rifting and associated hydrothermal mineral deposits leads to the deduction that determining the absolute age of sulfide mineralization will also elucidate the time of rifting. Although the age of rifting is reasonably well constrained by other geologic factors in this case, the ability of the Re-Os system to provide dates for sulfide minerals in sedimentary-hosted deposits may have considerable significance for regions with poor stratigraphic age constraints, such as with many Precambrian occurrences.

Re-Os Isotopic and Initial Os Isotopic Compositions:

An important observation regarding Re-Os systematics in pyrite is that different Red Dog ore samples yield highly variable $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios (Table 4), but preserve a well-correlated regression. Samples VP4 and VP5 are typical low-level highly radiogenic (LLHR) sulfides (Stein et al., 2001), in that they have relatively low Re and Os concentrations, but ^{187}Os comprises at least ~50% of the total Os present in the sample (Table 4). However, all other pyrite samples contain much more common Os, suggesting that the presence of Os in the ore-forming fluids in the Red Dog ore system

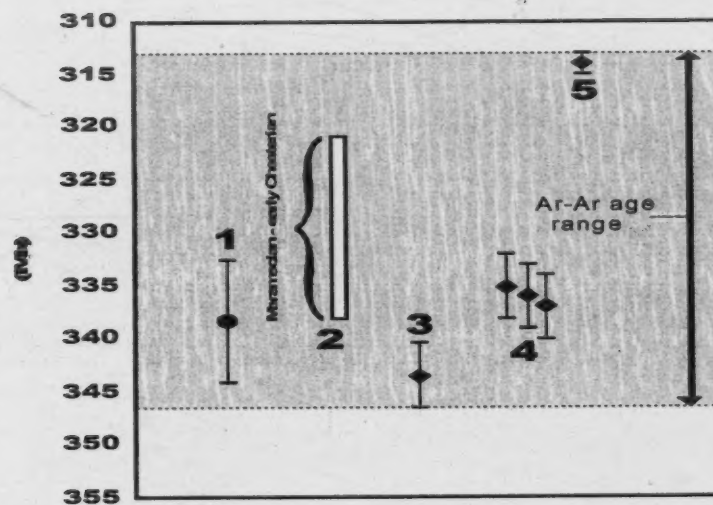


Figure 18: Age constraints for main stage mineralization at Red Dog: (1) Re-Os age for Red Dog main stage ore determined from massive and vein pyrite, (2) Conodont and radiolarian biostratigraphic age range (Dumoulin et al., 2004), (3) Ar-Ar biotite age from alkaline mafic igneous rocks near Red Dog that predate mineralization, (4) Drenchwater deposit maximum mineralization Ar-Ar age from biotite phenocrysts in alkaline intrusions cut by mineralization, (5) minimum mineralization (Ar-Ar hydrothermal white mica) age derived from igneous sill near Red Dog that is cut by sulfide-bearing vein, and thus predates mineralization (. (Note: all Ar-Ar ages from Werdon et al., 1997).

was highly variable. This may reflect variations in fluid chemistry (e.g. redox conditions, ligand chemistry) over time or in different portions of the deposit, or may be a result of variable sequestration of Re and Os from potential Re and Os sources, including the host shale. Alternatively, the incorporation of variable amounts of fluid-derived, Re- and/or Os-bearing micro-inclusions into the sulfides during mineral crystallization may explain the observed differences in Re-Os compositions.

The initial $^{187}\text{Os}/^{188}\text{Os}$ for main stage ore pyrite is determined to be 0.20 ± 0.21 from the pyrite regression line (Fig. 8). The imprecise nature on this value warrants considerable caution for any detailed interpretation, especially considering the lower uncertainty limit yields an impossible negative value. Notwithstanding this uncertainty, the initial $^{187}\text{Os}/^{188}\text{Os}$ value is rather low, even including the upper uncertainty limit of 0.41. Although this value does not preclude a mantle Os source, the low value makes it unlikely that a crustal reservoir(s) significantly older than the local stratigraphy at Red Dog ore could act as a potential Os source. For example, assuming an average upper continental crustal value of 48.1 for $^{187}\text{Re}/^{188}\text{Os}$ (Esser and Turekian, 1993), a chondritic initial $^{187}\text{Os}/^{188}\text{Os}$ for this hypothetical source, and using a ^{187}Re decay constant = $1.666 \times 10^{-11} \text{ yr}^{-1}$ (Smoliar et al., 1996), a maximum age of ~ 670 Ma is indicated. Performing the same calculation using the calculated initial $^{187}\text{Os}/^{188}\text{Os}$ value of 0.20 requires a maximum age of ~440 Ma for the source. This indicates that average crust between ~440 Ma and 670 Ma (Neoproterozoic – Early Phanerozoic) likely acted as a source of the Os present in the Red Dog main stage ore, if only a crustal Os source is considered.

Sphalerite as a Geochronometer:

The results of this study clearly indicate that, at present, the systematics of Re and Os in sphalerite are not sufficiently understood to warrant its use for geochronology, despite encouraging high and somewhat variable (167 – 568) Re/Os ratios. While the Re and Os compositions might be undisturbed in some sphalerite samples (e.g. MS136), some process, whether geologically or analytically based, has significantly affected others (e.g. MS139 and VS950). Reducing the sample size from 500 mg to 200 mg does not appear to change the result, so it seems doubtful that the Claus process within the Carius tube is responsible for the observed scatter. Furthermore, decoupling of Re and Os subsequent to mineral crystallization, as is observed for molybdenite (Stein et al., 1998b, 2001; Creaser and Selby, 2002), does not provide an explanation as the sphalerite samples used in this study were fine-grained and well homogenized. Perhaps the most plausible explanation is that Re and/or Os in sphalerite may be subject to mobilization or disturbance upon interaction with later hydrothermal fluids or during Brookian orogenesis, though these results clearly warrant the need for a more detailed study into the Re-Os isotopic systematics of sphalerite.

b) Meguma Deposits:

Implications of Re-Os ages for MGD Formation and Acadian Orogenesis in the Meguma Terrane:

Previous attempts at determining the absolute age of MGD gold mineralization (Kontak et al., 1990a, 1993; Kontak and Archibald, 2002) focused on $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology of hydrothermal vein micas and amphibole from several deposits,

including Upper Seal Harbour, Fifteen Mile Stream, Caribou, Moose River, West Gore, Beaver Dam, and Tangier (see figure 3 for locations). Results of these studies indicate a coincident but protracted episode of vein emplacement in the eastern Meguma Terrane at ca. 370 Ma (Kontak and Archibald, 2002). A similar timing of vein emplacement and gold mineralization for the southwestern Meguma Terrane is inferred (Horne and Culshaw, 2001; Kontak and Archibald, 2002) from a 376 Ma $^{40}\text{Ar}/^{39}\text{Ar}$ age for a muscovite pressure shadow surrounding arsenopyrite in a vein at The Ovens deposit (Hicks et al., 1999). Figure 19 indicates that an obvious discrepancy exists between Ar-Ar ages for gold mineralization and the Re-Os ages determined in this study. Although gold mineralization at Dufferin is <10 Ma older than suggested by the Ar-Ar data, the Re-Os data indicates that mineralization at The Ovens is ~30 Ma older than expected. Although it is possible that all Ar-Ar ages reflect a relatively later mineralizing event, a more probable explanation is that resetting of the Ar-Ar mica chronometers occurred at ca. 370 Ma, likely as a result of terrane-wide plutonism at this time.

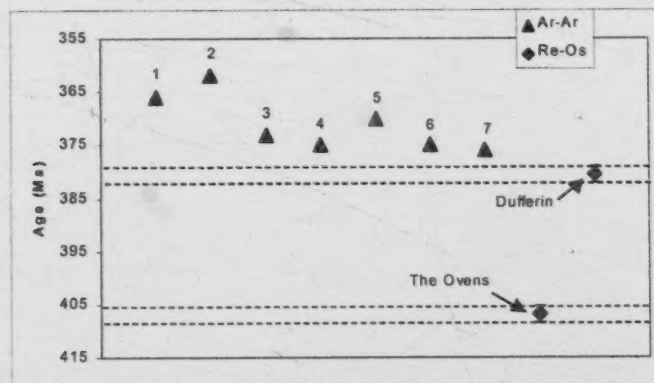


Figure 19: Comparison of Re-Os model ages of MGD determined in this study and Ar-Ar ages for various MGD, including (1) Upper Seal Harbour, (2) Fifteen Mile Stream, (3) Caribou, (4) Moose River (Kontak et al., 1990), (5) West Gore (Kontak et al., 1996), (6) Beaver Dam (Kontak et al., 1990; 1993), and (7) Tangier (Kontak et al., 2002).

Kontak and Archibald (2002) used several lines of reasoning to suggest that resetting of the Ar-Ar ages by later thermal events in the Meguma Terrane is unlikely. These include: variations in proximity of gold deposits to the ca. 370 Ma granites, older Ar-Ar ages for wall rock slate inclusions in veins (Kontak et al., 1998), and a lack of textural evidence for thermal influence of granites near deposits. However, the discrepancy between the Ar-Ar ages and the Re-Os ages determined here provides the first clear evidence that the Re-Os arsenopyrite chronometer is more robust than that of Ar-Ar with muscovite and biotite. This observation supports the hypothesis of Muecke et al. (1988), who use discordant $^{40}\text{Ar}/^{39}\text{Ar}$ mica, hornblende, and whole rock age spectrum data from the western Meguma Terrane to argue for Hercynian (385-360 Ma) and/or Alleghanian (320-300 Ma) overprinting of earlier events in this region.

Despite disagreement between the Re-Os and Ar-Ar ages, the Re-Os ages determined thus far concur with observations of mutually cross-cutting relationships between all vein types (Horne and Culshaw, 2001) and seemingly support gold mineralization models proposing the simultaneous emplacement of all vein types in the late-stages of regional folding, and that cite the ca. 370 Ma Ar-Ar mineralization ages as supporting evidence of this (Kontak et al., 1990b; Horne and Culshaw, 2001; see Table 1). This is based on the fact that, within 2σ uncertainty levels, the preliminary Re-Os ages for both bedding-parallel and bedding-discordant veins from a single deposit were identical, thus indicating a contemporaneous origin. However, several factors, including the current resolution of the Re-Os technique, the lack of age information for all discordant vein types, and uncertain age relationships between bedding-parallel veins

located in different portions of folds (e.g. limbs vs. hinge) at an individual deposit inhibit conclusive resolution of the 'correct' model of MGD formation using Re-Os isotopic data.

Despite identical Re-Os ages for veins from a single deposit, highly variable Re-Os ages from different deposits (i.e. The Ovens vs. Dufferin) suggest that gold mineralization was not concurrent from place to place within the Meguma Terrane. This may be explained in two ways:

(1) Disregarding the exact timing, the summary of models in Table 1 indicates that the majority of existing models promote an association between formation of the deposits and a discrete tectonic (deformational) stage. Therefore, the ca. 26 Ma age difference between the two deposits suggest that the appropriate physiochemical conditions favourable for MGD formation were attained at different times across the Meguma Terrane, and that Acadian orogenesis was a diachronous event in the region. Perhaps this conclusion is not surprising, considering that the Meguma Terrane was the largest of all terranes accreted during the Appalachian Orogeny ($\sim 200,000 \text{ km}^2$; Schenk, 1995), the collision was associated with oblique convergence (Keppie and Dallmeyer, 1995), and that such a diachrony has previously been proposed for different regions of the northern Appalachians affected by Acadian orogenesis, including the Dunnage Zone (Tremblay et al., 2000), the northeastern U.S.A. (Robinson et al., 1998; Eusden, Jr., et al., 2000; Bradley et al., 2001; West et al., 2001), and the Meguma Terrane itself (Keppie and Dallmeyer, 1987; Keppie, 1993; Kontak et al., 1998; Murphy et al., 1999). Figure 20 displays a comparison between the Re-Os ages determined here and existing age data constraining the duration of Acadian orogenesis in other regions of the northern Appalachians, as well as age information for distinct tectonic events within the Meguma

Terrane. The accuracy of the Re-Os arsenopyrite ages is also evident in Fig. 20, as they overlap consistently with independent age constraints for regional metamorphism in the Meguma Terrane, and correlate well with existing age constraints for diachronous Acadian orogenesis in the Meguma Terrane and elsewhere in the northern Appalachians.

(2) An alternative explanation for the difference in Re-Os ages stems from models that propose the possibility that different vein-types were introduced at different times during orogenesis (e.g. Williams and Hy, 1990). In this regard, it may be concluded from the Re-Os data that deposits dominated by bedding-parallel and -discordant veins in fold limbs, such as The Ovens, represent a primary mineralizing event in the Meguma Terrane, whereas veins concentrated in fold hinges (i.e. saddle-reef veins), such as Dufferin, represent a much later influx of mineralizing fluids into fold hinges, possibly associated with reactivation of pre-existing fold structures.

MGD Source Characteristics from Re-Os Ages and Initial Re-Os Isotopic Compositions:

The determined initial Os isotopic composition ($^{187}\text{Os}/^{188}\text{Os}$) of arsenopyrite from The Ovens deposit is 0.82 ± 0.16 (Fig. 12), whereas analyses of Dufferin deposit arsenopyrite yields a somewhat lower initial Os value of 0.37 ± 0.14 (Fig. 15). Although the initial Re-Os isotopic compositions cannot alone be used to characterize the exact source of the fluid(s) responsible for MGD formation, they can be used along with age information to eliminate some possibilities.

Based on the determined initial Os compositions, it is clear that the fluid(s) must be, in large part, crustally-derived, as chondritic $^{187}\text{Os}/^{188}\text{Os}$ values are ~ 0.127 for the early Devonian (ca. 400 Ma), substantially less radiogenic than the determined

arsenopyrite initial Os values for both deposits. The variability in initial Os compositions from The Ovens and Dufferin suggests either (1) variability in the chemical composition of a single source from place to place within the Meguma Terrane, (2) variation in characteristics of the same source over time, (3) a different source for younger deposits, or (4) a variable mixture between two components – a principal one with high $^{187}\text{Os}/^{188}\text{Os}$ (older crust), and a subordinate one with a much lower $^{187}\text{Os}/^{188}\text{Os}$ (juvenile crust? / mantle?) - at some of the deposits.

Several potential crustal sources exist within the Meguma Terrane and/or its underlying basement, with the most cited possibilities being the Meguma Group sediments themselves, the ca. 370 Ma granitic intrusions, and the sub-Meguma Group lower crust (represented by xenoliths in late Devonian lamprophyres and by the Liscomb Complex). It is difficult to discriminate between these possible sources using the determined initial Os isotopic compositions, especially considering the lack of information on Os isotopic compositions for these potential sources. It is unlikely, however, that the ca. 370 Ma granitic intrusions played a significant role in the formation of the MGD. Although the 381 Ma Re-Os arsenopyrite age from Dufferin overlaps the earliest pluton emplacement ages (Fig. 20), the Re-Os age of The Ovens arsenopyrite clearly predates pluton emplacement, indicating that they were not an integral component in the formation of the gold deposits. Therefore, the most likely candidates for the source of mineralizing fluids based solely on the Re-Os data are the Meguma Group sediments or metamorphic fluids derived from the lower crust, with possible contributions from the mantle or from younger crust at some deposits.

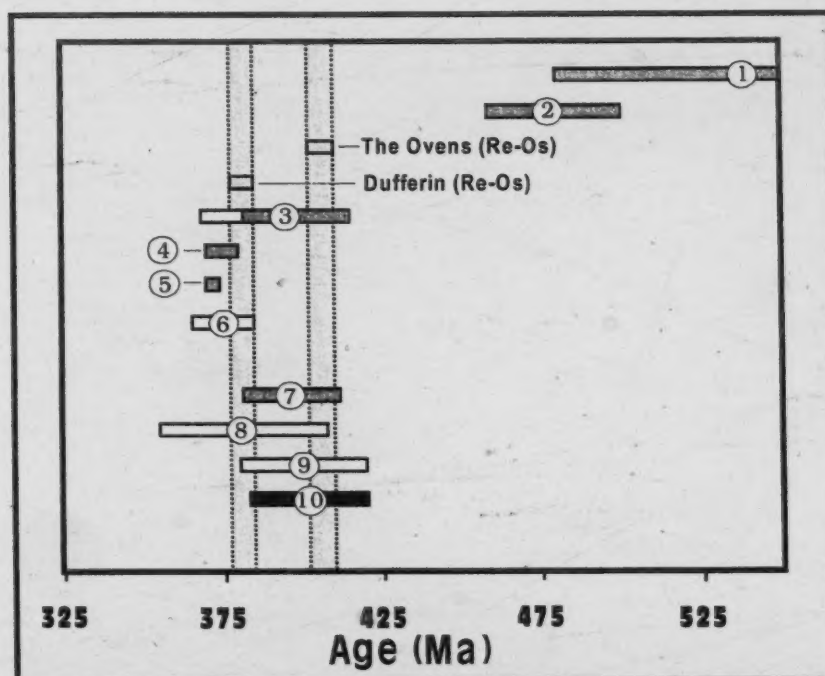


Figure 20: Comparison of Re-Os ages with compilations of existing age data constraining the duration of tectonic events in the Meguma Terrane and Acadian orogenesis in the northern Appalachians; grey shading denotes K-Ar (whole rock) or $^{40}\text{Ar}/^{39}\text{Ar}$ (mica), white denotes U-Pb (monazite, zircon), and black denotes integration of 3 or more dating techniques: (1) deposition of Goldenville Fm. (Poole, 1971; Hicks et al., 1999), (2) deposition/diagenesis of Halifax Group (Lambert et al., 1984; Cumming et al., 1985; Hicks et al., 1999), (3) regional metamorphism (Reynolds et al., 1998; Muecke et al., 1988; Kontak et al., 1998; Hicks et al., 1999; Greenough et al., 1999), (4) emplacement of Liscomb Complex (Kontak and Reynolds, 1994), (5) emplacement of lamprophyre dykes (Kempster et al., 1989; Clarke et al., 1997), (6) emplacement of granitic plutons (Fallon et al., 2001; Kontak et al., 2003), (7) diachronous cooling across Meguma Terrane (Keppie and Dallmeyer, 1987; Kontak et al., 1998, and references therein), (8) duration of Acadian deformation across New Hampshire (Eusden et al., 2000), (9) Acadian metamorphism across east-central Maine (West et al., 2001), (10) migration of Acadian Orogeny across Maine (Bradley et al., 2001).

Arsenopyrite as a Chronometer for Au Mineralization:

Arne et al. (2001) performed a preliminary investigation into the use of arsenopyrite for Re-Os geochronology by analyzing two arsenopyrite samples from the Bendigo goldfields in Central Victoria, Australia. In this study, a combined arsenopyrite-pyrite isochron was constructed and single-mineral model ages were calculated for two arsenopyrite samples in order to determine the age of gold mineralization at Bendigo.

The present study confirms the results of Arne et al. (2001) by validating Re-Os geochronology of arsenopyrite as a reliable means of dating associated gold mineralization, and builds on their work by providing a more detailed analysis of the theoretical and analytical limitations of the chronometer.

Arsenopyrite from the MGD are characterized by much more variable Re and Os isotopic compositions than the Bendigo samples, as their $^{187}\text{Re}/^{188}\text{Os}$ ratios ranged from ~800 to 275000, compared to a more limited range of ~1700 to 2200 for the Bendigo samples. Calculation of precise single-mineral model ages assuming no initial Os was possible for the MGD samples with extremely high $^{187}\text{Re}/^{188}\text{Os}$ ratios, thereby eliminating the need for use of an assumed initial $^{187}\text{Os}/^{188}\text{Os}$ ratio, such as is done for the Bendigo samples. Figure 17, a comparison between all Re-Os ages determined in this study for the Dufferin deposit, shows the advantage of using samples with extremely high Re/Os ratios over those characterized by much lower Re/Os ratios. It is clear from this comparison that those samples with the lowest Re/Os ratios (D6-1, -2) yield the least accurate and least precise model ages. This is due solely to the fact that inaccuracy in the assumed initial Os isotopic composition has a much larger effect on the age determined for these samples, whereas for samples with extremely high Re/Os ratios (i.e. less initial

Os), the effects are negligible. Furthermore, the use of an isotopically normal Os spike with these samples rather than a single isotope Os spike permits for isotope fractionation corrections to be made, and provides a check on the determined age using an independent methodology. This combination of factors allows for the determination of extremely accurate and precise single-mineral model ages.

Previous studies on Re-Os chronology with molybdenite (Stein et al., 1998b, 2001; Creaser and Selby, 2002) recognized a decoupling between Re and Os within the molybdenite crystal, such that analysis of different portions of a single crystal would yield widely variable ages. The present study was able to establish that this phenomenon does not occur within the arsenopyrite crystal structure, as separate analyses (OV5a and OV5b) of different portions of single arsenopyrite crystals yield identical ages.

Additionally, the relationship between sample size and the possible effects of the Claus process for arsenopyrite were addressed during the course of this study. In order to minimize the effects of the Claus process for Carius tube dissolution of pyrite, Frei et al. (1995) suggest a maximum sample size of ~200 mg. However, results of the MGD samples indicate that (along with an increase in the volume of HNO_3 in the inverse aqua regia from 6ml to 9ml) a sample size of 500 mg of arsenopyrite may be used per individual analysis. This is concluded due to the results from analyses of samples D4a-1 and D4a-2, which yield identical model ages (381 Ma) despite sample weights of 200 mg and 513 mg, respectively.

The combination of factors and results discussed above will prove crucial for future work with Re-Os arsenopyrite geochronology, in that they will direct sampling techniques, analytical protocol, and theoretical considerations. Considering the common

association between cogenetic gold and arsenopyrite in lode gold deposits, the reliability of the Re-Os arsenopyrite chronometer as proven by this study, and the technical advancements described above, Re-Os arsenopyrite geochronology could become the foremost analytical tool for distinguishing the timing of quartz-vein hosted gold mineralization.

Chapter 6 - Conclusions:

The results of this study conclusively demonstrate the feasibility and reliability of Re-Os pyrite and arsenopyrite geochronology for dating ore-forming events.

Combined Re-Os analyses of pyrite from vein sulfide and massive sulfide ore from main stage ore at the Red Dog deposit, Alaska, yield a Model 3 isochron age of 338.3 ± 5.8 Ma, consistent with independent $^{40}\text{Ar}/^{39}\text{Ar}$ and biostratigraphic age constraints. This age is here interpreted to represent the age of main stage ore mineralization at Red Dog, and exhibits a cogenetic relationship for massive sulfide and sulfide vein ore facies. Additionally, it is suggested that the Re-Os age reflects the depositional age of sedimentary units correlative to this synsedimentary deposit, and the age of rifting responsible for basin development and deposit formation. Re-Os analyses of sphalerite from Red Dog yields erroneous and imprecise ages, thus implying that the Re and/or Os isotopic systematics are easily disturbed in sphalerite, and that pyrite is more robust than sphalerite in this regard.

Additionally, the precise timing of lode gold mineralization from the Meguma Group deposits, Meguma Terrane, Nova Scotia is elucidated using Re-Os chronometry of cogenetic arsenopyrite. Re-Os isotopic ratios are very variable between different samples,

thus requiring meticulous data treatment for age determination. Analyses of arsenopyrite from bedding-parallel veins at The Ovens deposit yield an $^{187}\text{Re}/^{187}\text{Os}$ vs. $^{187}\text{Os}/^{187}\text{Os}$ isochron age of 408.6 ± 4.5 Ma, whereas analysis of arsenopyrite from a bedding-discordant vein, characterized by a much higher $^{187}\text{Re}/^{187}\text{Os}$ isotopic composition (i.e. much less initial Os) than for the bedding-parallel samples, yields a fractionation-corrected single-mineral model age of 406.9 ± 1.7 Ma. Regression of arsenopyrite Re-Os analyses from both vein types yields an $^{187}\text{Re}/^{187}\text{Os}$ vs. $^{187}\text{Os}/^{187}\text{Os}$ isochron age of 407.0 ± 4.1 Ma and an ^{187}Re vs. ^{187}Os isochron age of 406 ± 28 Ma. This suggests that both vein-types and associated Au mineralization were emplaced simultaneously, thus placing rigid timing constraints on models of deposit formation.

Alternatively, arsenopyrite Re-Os analyses from saddle-reef veins at the Dufferin deposit yield an $^{187}\text{Re}/^{187}\text{Os}$ vs. $^{187}\text{Os}/^{187}\text{Os}$ isochron age of 381.1 ± 2.8 Ma, an ^{187}Re vs. ^{187}Os isochron age of 390 ± 24 Ma, and a fractionation-corrected single-mineral model age of 380.6 ± 1.5 Ma. The much younger age of the Dufferin saddle-reef vein arsenopyrite relative to bedding-parallel and -discordant vein arsenopyrite from The Ovens suggests either a diachronous evolution of the Acadian Orogeny across the Meguma Terrane, or else the emplacement of a much later influx of gold-bearing fluids into pre-existing fold hinges.

The results of this study conclusively exhibit the effectiveness of Re-Os pyrite and, more impressively, arsenopyrite for dating ore-forming events. Arsenopyrite, a common accessory mineral in many lode gold deposits, has here been proven a more robust chronometer than Ar-Ar mica. Furthermore, the discovery of arsenopyrite crystals with no common Os allows for the calculation of single-mineral model ages without prior

knowledge of the initial Os composition, identical to the technique used for Re-Os molybdenite geochronology. The results of this study clearly move Re-Os pyrite and arsenopyrite geochronology to the forefront of analytical tools which aid in the understanding of and exploration for metalliferous ore deposits.

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Appendix 1:

Equation used for calculation of 'rho':

$$\rho (rho) = \frac{\left(\frac{\sigma_{(^{187}\text{Re}/^{187}\text{Os})}}{^{187}\text{Re}/^{188}\text{Os}} \right)^2 + \left(\frac{\sigma_{(^{187}\text{Os}/^{188}\text{Os})}}{^{187}\text{Os}/^{188}\text{Os}} \right)^2 - \left(\frac{\sigma_{(^{187}\text{Os}/^{187}\text{Re})}}{^{187}\text{Os}/^{187}\text{Re}} \right)^2}{2 * \frac{\sigma_{(^{187}\text{Re}/^{188}\text{Os})}}{^{187}\text{Re}/^{188}\text{Os}} * \frac{\sigma_{(^{187}\text{Os}/^{188}\text{Os})}}{^{187}\text{Os}/^{188}\text{Os}}}$$

where σ denotes 1 sigma uncertainty in measurement.